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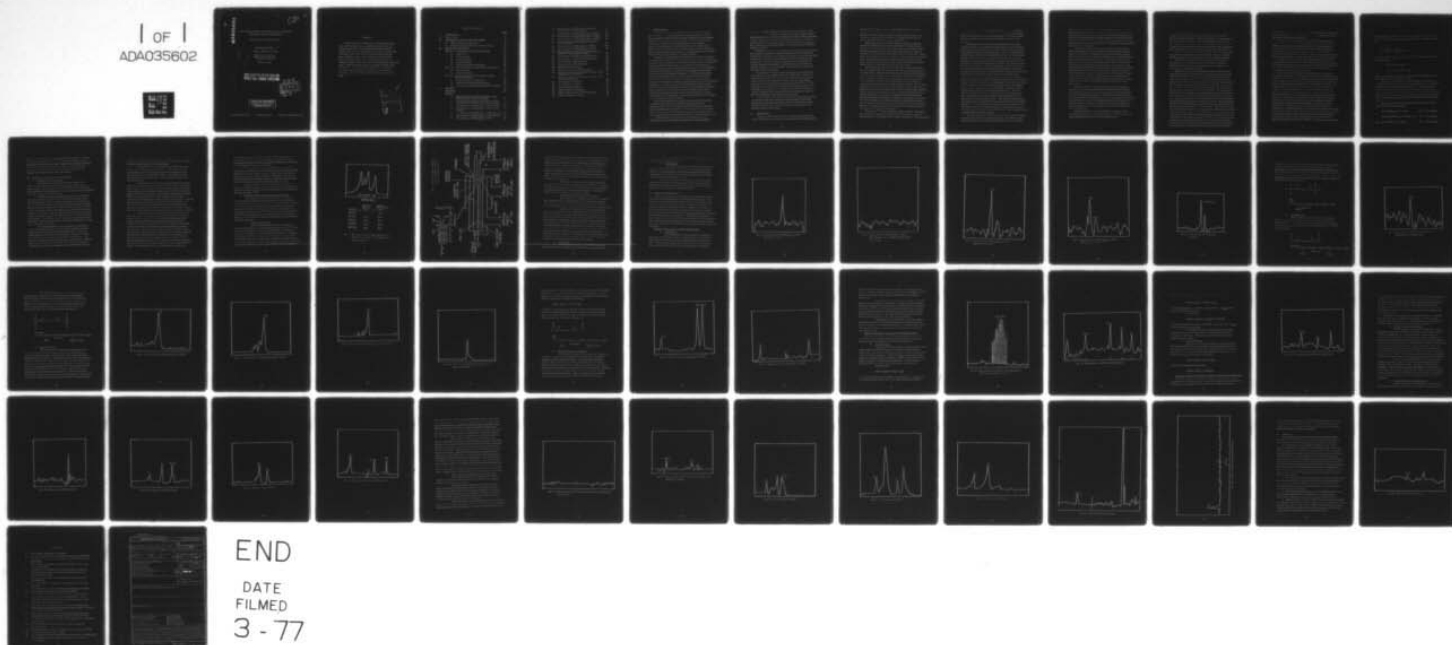   NOV 76   M FARBER, R D SRIVASTAVA   N00014-75-C-0986
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A MASS SPECTROMETER INVESTIGATION OF THE CHEMISTRY
OF PLATEAU BURNING PROPELLANTS

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ABSTRACT

A mass spectrometer study has been conducted involving double base plateau burning propellants containing lead and copper organic salts. The pyrolysis and combustion of the metallic salts were also investigated. The results revealed that the metallic salts decompose to the gaseous and condensed phase metallic elements. The gaseous lead or copper atoms then react with the nitrate esters to form compounds such as $PbNO_2$ and $CuNO_2$, which are stable in the intermediate temperature zones. When the nitrites enter the combustion zone they react to produce the metallic hydroxides and oxides as predicted by the thermodynamic equilibria. The formation of the $PbNO_2$ and $CuNO_2$ may be the criterion for the mechanism of the mesa effect.

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I. INTRODUCTION

This report presents the results of a mass spectrometer study of the chemistry of super-rate and plateau burning propellants. Double base propellants containing lead and copper additives were investigated. Experiments were performed to determine the mechanisms and reactions resulting when organic lead or copper compounds were added to nitrate ester propellants. This investigation was conducted in three phases: (1) decomposition studies of organic lead and copper additives; (2) combustion studies of the additives in an H_2/O_2 flame; and (3) studies of the reactions of the propellant itself after ignition.

Previously, various experimental studies were conducted involving lead compound catalyzed double base propellants, including investigations concerning heat of explosion, strand burning, rocket motors, and others.[1-12] The data heretofore reported indicate that the key to establishing the mechanism for super-rate and plateau burning may lie in the understanding of the reactions taking place between the lead additive and the nitrate ester prior to high temperature combustion. Thermocouples imbedded in the solid propellant below the burning surface have indicated that some types of reactions occur prior to combustion, showing a higher temperature for propellants containing lead additives than for the unmodified propellants. In addition, several investigative groups found that the heat of combustion was higher in the case of the lead additive propellant. This may have been due to either the direct combustion of the lead compound forming higher energy acidic or oxide compounds, or to the combustion of a lead intermediate, as suggested by Suh, et al,[6] resulting in more energetic combustion products.

It has been shown that no plateau is formed when the propellant is burned at high pressures, resulting in higher temperatures, suggesting that at these high temperatures the intermediate compounds which would normally result from the reaction between the lead additive and the ester are not formed; instead, both the lead compound and the nitrate ester are consumed individually and thus no plateau burning occurs.

Several hypotheses and theoretical mechanisms have been advanced for super-rate and plateau burning lead compound additive

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propellants. Based on previous investigations, these include: (1) the formation of a complex between the chelate lead atom and alkyl nitrate;[6] (2) radiation absorbed into the propellant from the flame;[7] (3) the reduction of NO by catalysis action of the lead compound acting in conjunction with the carbon on the burning surface;[1,4] (4) the exothermic reduction of NO_2 to NO with accompanying oxidation of C,H,O species;[5] and (5) the formation of NO_3.[3]

Although these previous investigations offered conclusions regarding the mechanisms involved, no general agreement has been reached and therefore the chemical causes of plateau burning have remained unresolved. Specifically, uncertainties and disagreements exist pertaining to the mechanisms which produce plateau burning when lead compounds are added to double base propellants, the identification of the pre-flame products involving the lead and double base components, and the lead compound combustion products.

The results of the present study indicate that the decomposition of the organic metallic additive yields the metallic atom, whether in a condensed or gaseous phase. The gaseous lead atom reacts with the nitrate ester in the precombustion, or fizz, zone to produce $PbNO_2$, which remains stable at moderate temperatures (below $1000^{\circ}C$). In the combustion zone the $PbNO_2$ is consumed and the classical products of combustion, PbO, PbO_2, etc., are formed. The removal of NO_2 as a reactant at moderate pressures and at the lower temperatures may be a factor in the formation of the plateau burning region.

A brief summary of the results of other experimental investigations, a description of the mass spectrometer and four-stage differentially pumped mass spectrometer apparatus, and a discussion of the results obtained in the investigation at this laboratory are presented in the following sections of this report.

II.   BACKGROUND

Numerous investigations have been conducted to determine the causes, and to propose mechanisms, for super-rate and plateau burning

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propellants.[1-12] These programs have included research on strand burning, heats of explosion, combustion gas analysis, and temperature and pressure profile studies of double base propellants modified with 1 to 2% lead compound concentrations. A summary of the results of several of these investigations is presented below.

Early work on the use of metal additives to produce super-rate and plateau burning has been reported by Preckel,[1] who found that the addition of certain lead compounds to nitrocellulose propellants tended to limit the burning rate at pressure levels below 5000 psi. Plateaus were formed at lead stannate concentrations between 0.5 and 1%. Higher lead salt concentrations moved the plateau to lower pressures and burning rates. He found that aliphatic lead salts resulted in plateau burning at low pressures with low burning rates, while aromatic lead salts gave plateau burning at high pressures with high burning rates.

Preckel made photomicrographs of the burning propellant surfaces and of the sloughed off carbonaceous debris during strand burning tests in a closed bomb. Globules of molten lead were observed at all pressures below the upper limit of the plateau but did not appear above the plateau limit. He hypothesized that the catalytic action of the lead compound could well involve only the oxygen-containing species in either the condensed or the gaseous phase directly above the surface. The accepted mechanism of nitrate ester decomposition to NO_2 and to the RO' radical, followed by the reduction of NO_2 to NO, and the eventual slower reduction of NO to N_2, has been thought to involve a catalytic cycle of reactions with Pb and PbO; Pb is assumed to be oxidized by NO or NO_2 and the resultant PbO reacts with oxidizable molecules or fragments to regenerate Pb. Preckel stated that this action could occur either in the gas phase or in a condensed zone in the extreme outer layers of the burning material. However, he reported that although this mechanism appeared appropriate, it had not been conclusively established.

Camp, et al,[11,12] have presented a condensed phase hypothesis, proposing that the adsorption of radiation below the burning surface of the propellant is a significant factor in super-rate burning. Their explanation

is that the plateau burning phenomenon is produced as a result of the
formation of agglomerated globules of lead metal on the burning surface
which shield the surface from absorbing radiation. They also suggest
that the accumulation of lead metal on the surface increases with
pressure.

Lenchitz and Haywood[2] studied photographically the burning
surfaces of double base propellant strands modified with lead additives.
They found that at burning pressures of 150 lb/in^2 the burning surface
of the modified propellant was homogeneous, was well formed and had
a uniform glow. The non-modified propellant surface showed localized
pockets of reaction, with hot particles being ejected intermittently.
In addition, the final gas pressure of the modified propellant exceeded
that of the non-modified propellant at 150 lb/in^2. This difference was,
however, too small to be considered significant and could not be used
as a definite indication of the completeness of reaction. The higher
burning rate of the modified propellant therefore indicated that the surface
reaction in the modified propellant was more energetic and not as
dependent on heat feedback from the flame as was the non-modified
propellant. Differences in flame structure disappeared beyond the plateau
region. Here the burning rate was significantly influenced by the transfer
of heat caused by the large temperature gradient between the surface
and the flame. They concluded that in addition to inducing chemical
changes at low pressure with corresponding changes in $\triangle Q$, lead
stearate may have affected the completeness of the reaction; that is,
when $\triangle Q$ changed with pressure it was assumed that lead stearate
influenced the chemistry of the reaction. The chemical analysis of the
gases showed that the CO_2/CO ratio was nearly that of the non-additive
propellant. However, the authors stated that it was possible that the
lead stearate induced simultaneous changes in the physical aspects of
the burning process. They felt that the complexity of the burning reactions
precluded any quantitative estimates.

Dauerman and Tajima[3] studied the decomposition of nitrocellulose
separately and with 2% lead stearate additives. The additive caused
an increase in the NO_3 concentration (although NO_3 was not directly

observed) at burning rate pressures as low as 10 torr, thereby increasing the oxidation potential of the reactions. The supporting experimental observations were: (1) an increased regression rate; (2) a higher overall chemical activity; and (3) an increased oxidation rate of C-H-O species by NO_3 and, possibly, by NO_2. They thus determined that the increased regression rate was due to the faster rate of oxidation-reduction reactions induced by the lead catalyst.

A second conclusion based on their studies was that nitrogen dioxide apparently was not the initial decomposition product of solid double base propellants. Furthermore, NO rather than NO_2 appeared to be formed when NO_3 was reduced, and NO_2 was not a primary product from decomposition of cellulose nitrate. They stated that Adams and Wiseman [13] had also made this determination earlier. Dauerman and Tajima further concluded that the predominance of nitric oxide as the volatized species indicated that NO_2 reacted very rapidly in the thermal zone of nitrocellulose if it was indeed formed initially by rupture of the $CO-NO_2$ bond. NO_2 was complexed as the nitrate group ($CONO_2$), or complexed immediately as it was formed when nitrocellulose was heated and then reacted very rapidly, leading to the formation of highly oxidized species such as H_2O, CO, CO_2 and carbonyl and acidic intermediates.

Dauerman and Tajima included a comment in their publication that the reviewers had suggested that their failure to observe NO_2 as the predominant species did not necessarily mean that the initial step was not a CO_2-NO_2 bond scission. The reviewer's argument was that the NO_2 formed would initially dissolve in the nitrocellulose and oxidation processes leading to the reduction product NO would take place in the condensed phase. However, it should be noted that no attempt was made to determine the lead intermediates or any reactions involving the lead compounds.

Heller and Gordon [10] have concluded from gas phase studies of double base propellants that reactions between the nitric oxides and organic hydrocarbons occur in the foam and fizz zones.

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Hewkin, et al,[4] proposed that the cause for plateau burning resulted from the lead additive generating carbonaceous matter at or near the propellant surface. This in turn induced a reaction between NO and any of the reactant species in the vicinity, such as H_2, C, CO, aldehydic moieties, etc. However, if this were the mechanism it would be anticipated that larger quantities of $CO + CO_2$ would appear in the final products since charcoal reacts with NO to form $CO_2 + N_2$.

Hewkin, et al, found that Fe_2O_3, CO_2O_3, CuO, ZnO, SnO_2 and Al_2O_3 increased the burning rate with pressure. However, PbO was the only metal oxide which produced super-rate and plateau burning.

Salooja[9] reported that whereas PbO inhibits the combustion of hydrocarbons, it strongly promotes the combustion of oxygen derivatives of hydrocarbons such as formaldehyde, acetates, etc., thus increasing the formation of CO_2.

Kubota, et al,[5] investigated various metallic, metal oxide and metal organic additives to nitrocellulose and trimethylolethane nitrate (TMETN) propellants. The lead organic salt additives produced both super-rate and plateau burning. The regions directly affected by the lead compound were the condensed phase just below the burning surface and the burning surface itself (a distance less than 100μ at 1 atm and 20μ at 20 atm), where the lead compounds decomposed ultimately into finely divided metallic lead or lead oxide products. The decomposition products of the lead catalyst reacted with nitrate esters in this surface reaction layer where the chemical degradation goes to NO_2, aldehydes, etc., altering their normal thermal decomposition paths so as to produce an increased amount of carbon at the burning surface. Most importantly, the presence of lead compounds resulted in a strong acceleration of the fizz zone reactions (within 100μ of the surface). The result of the fizz reaction rate acceleration was an increased heat feedback which produced super-rate burning. Kubota, et al, concluded that this action of the lead compounds to produce increased carbon and the acceleration of the fizz zone reactions were directly coupled. The portion of decomposed organic molecules which appeared at the surface in the form of carbon rather than readily oxidizable aldehydes could have reduced the effective fuel to oxidizer ratio, constituting a shift in equivalence ratio toward the

stoichiometric value. Such a shift in NO_2/aldehyde mixtures would result in a greatly accelerated reaction rate (their proposed mechanism for the fizz zone reaction rate acceleration).

Kubota, et al, explained the plateau effect by theorizing that as the burning rate increased the time available for the initial catalytic action in the surface reaction layer decreased. Thus the fraction of reactants affected by lead compounds and increased NO_2 decreased in the fizz zone with increased burning rate. That is, the super-rate burning diminished as pressure increased. The rate of super-rate burning with increased pressure determined the slope of the burning rate plateau.

This theory, however, differs from that of Hewkin, et al,[4] who reported that carbon catalyzed the NO reduction in the fizz zone; Kubota, et al, stated that, instead, lead compounds increased the NO_2 concentration entering the fizz zone which in turn accelerated the gas phase reactions which utilize NO_2 as the oxidizer.

Suh, et al,[6] in investigating the addition of lead compounds to double base propellants, also found that imbedded thermocouples showed a hotter region at the surface of propellants containing lead salicylaldehyde or lead stannate. The Q value for the modified propellant was higher than for the unmodified propellant (608 cal/g vs. 532 cal/g at 150 psi). Their analysis of the gaseous products of combustion at 200 psi showed that in all the modified propellants the concentration of NO was reduced. For the lead stannate propellants the NO was reduced to one-half but the CO and CO_2 were the same for both the modified and the unmodified propellants. Suh, et al, proposed that the lead modifier increased the burning rate in the lower region of pressure by expediting the initial decomposition reaction through the reduction of energy of either the $RO-NO_2$ or the $R-ONO_2$ bond. It was assumed that the lead in the modifier was in plumbous condition, where it formed a number of compounds. They suggested that the formation of the complex involving the nitro moiety weakened the $RO-NO_2$ bond, leading to an increase in the burning rate by expediting the dissociation of the nitrate ester. All of the lead salts which would thus modify the propellant, causing super-rate burning,

contain chelating compounds. Suh, et al, envisioned a complex formed
between the chelate, a lead atom, and alkyl nitrate, possibly structured
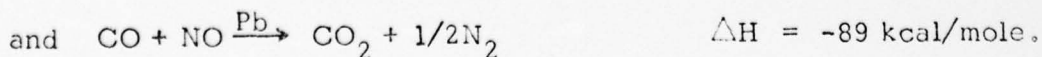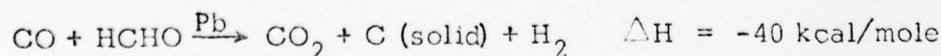as
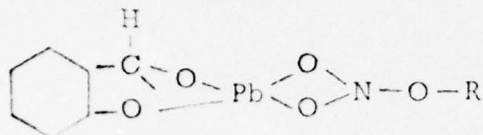
This conflicts with Preckel's hypothesis[1] in which the lead reduces the
NO catalytically,

$$Pb^* + NO \longrightarrow PbO$$

$$PbO + C \longrightarrow Pb^* + CO.$$
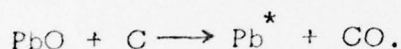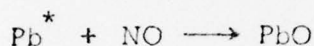
Suh, et al, felt that the reduction in NO was in all probability caused
by its reaction with H_2 to form $N_2 + H_2O$.

Thus Suh, et al, concluded that the ballistic modifier affected
the initial step in the decomposition of NC propellants via an electronic
interaction between the lead compound and NC. This was supported
by their thermocouple and calorimetric measurements at low pressure
where condensed phase reactions dominated. Their hypothesis predicted
that modifiers such as lead salicylate producing chelate type compounds
do cause super-rate burning, while lead tetraphenyl (covalent bonded)
do not.

Fifer and Lannon[8] proposed that the Pb catalyzes the formation
of CO_2 in the following reactions:

$$CO + CO \xrightarrow{Pb} CO_2 + C \text{ (solid)} \qquad \Delta H = -41 \text{ kcal/mole}$$

$$CO + HCHO \xrightarrow{Pb} CO_2 + C \text{ (solid)} + H_2 \qquad \Delta H = -40 \text{ kcal/mole}$$

$$\text{and} \quad CO + NO \xrightarrow{Pb} CO_2 + 1/2 N_2 \qquad \Delta H = -89 \text{ kcal/mole.}$$

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Since these are exothermic, they lead to higher temperatures. They are not in agreement with Camp, et al,[11,12] that the catalytic activity is located in the secondary flame zone. Rather, they suggest that catalysis takes place mainly in or on the burning surface, or in the fizz zone. They disagree with the chelate hypothesis on the basis that a non-chelate such as PbO can cause super-rate burning.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

A. Mass Spectrometer Apparatus

The apparatus consists of two separate entities. The first section is the high temperature vacuum furnace for heating the various reaction cells to temperatures up to $2500^{\circ}K$. The second is the mass spectrometer vacuum chamber in which a quadrupole mass spectrometer is held in a high vacuum (10^{-9} mm Hg).

The furnace chamber is fabricated in a cross configuration using 304L stainless steel 12" and 3 1/2" diameter schedule 10 pipe and 3/8" thick plate. The mass spectrometer system seals off one of the 12" pipes, while the other 12" flange supports the furnace assembly. During the furnace operation the 12" pipe is cooled with Freon 22 which is expanded through a coil of 5/8" copper tubing soldered to the outside surface of the 12" pipe. Each 12" flange is air cooled using high speed blowers. The furnace chamber is evacuated by a 4" high speed diffusion pump (750 l/s). The diffusion pump is backed by a two-stage forepump (100 l/min). Both an expanded water cooled chevron baffle and a 4" cold trap are included in the system.

The mass spectrometer vacuum chamber is constructed in a cross configuration using 5" and 3 1/2" 304L stainless steel pipe. The pumping system consists of a CVC diffusion pump, a Granville-Phillips Cryosorb cold trap and a Cenco Hyvac 7 forepump. A vacuum of 1×10^{-9} mm Hg is obtained in the chamber without bakeout. The reaction cell and flow system are mounted on a separate plate, which is sealed to the main flange by an O-ring. This arrangement facilitates the maintenance of the reaction system without disturbing the furnace

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assembly. By means of two liter gas ballast tanks the reaction gas is maintained at constant pressure during an experiment (only 1% reduction in tank pressure during a one-hour experiment).

The quadrupole mass spectrometer (model Quad 200 manufactured by Electronic Associates, Inc.) has a resolution of 500 and a sensitivity of 10^{-14} torr for N_2 when an electron multiplier is used in conjunction with an electrometer amplifier. The quadrupole probe, factory mounted on a 4" Ultek flange, projects approximately 9" into the vacuum system.

The detection of a gas species in a molecular beam by mass spectrometric measurement is limited by the interference of background gases at the same m/e number. Since the molecular beam cross-section is only a fraction of 4π steradians at the ionizer ($\sim 10^{-4}$) the effective species "pressure" in the beam is consequently attenuated by this factor relative to the background gases. This interference reduction is accomplished by providing the separate pumping chambers where a 100-fold pressure difference can be maintained between the two chambers. In addition, the use of a tube instead of an orifice in the effusion cell providing a molecular beam diminishes the number of off-angle molecules that arrive at the ionizer, thus reducing the pressure in the source chamber.

Ion currents which originate from species in the molecular beam appear as a 30 c/s square wave while background gases continue to exist as a d.c. current. The output signal from the electrometer amplifier is fed to a Princeton Applied Research Model JB4 lock-in amplifier. The reference signal for the lock-in amplifier is derived from a signal generated by passing two miniature magnets past a magnetic recording head. These magnets are held radially in an aluminum disc, attached to the shaft of the motor. Minor adjustments in the phase angle are effected by a delay circuit in the reference wave generator. The detection limit of the electron multiplier current achieved is 10^{-13} A, which is equivalent to a few ions s^{-1} arriving at the electron multiplier. In addition, an a.c. current can be observed in a d.c. signal 1000 times greater. To ascertain the source of the chopped ion a sector with

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several holes ranging from 1/16" to 7/32" in 1/32" steps can be rotated in the beam path. Species which originate solely from the cell show no significant attenuation with hole sizes 1/8" and above. This sector is approximately 3" from the reaction cell.

The resolution of the mass spectrometer is 1 in 500 amu. The effective resolution can be seen from an examination of the isotopic distribution of a large tungsten molecule, WF_6, as shown in Figure 1. This figure shows the relative intensities of WF_5^+ (the major species in the cracking pattern of WF_6), which are in excellent agreement with the known relative percentages of the four tungsten isotopes.

Additional furnace and mass spectrometer details, as well as methods of calculation for obtaining species and concentrations from the dual vacuum furnace and mass spectrometer system have been presented previously.[14,15]

B.   Four-Stage Differentially Pumped Vacuum System

To accomplish the operation of a flame at a pressure of one atmosphere and at the same time obtain the mass spectra of the combustion "frozen" species produced in the atmospheric flame required the construction and assembly of a four-stage differentially pumped vacuum system. This system provides a pressure variation from one atmosphere in the flame to 10^{-11} atmospheres at the mass spectrometer. The four-stage differential vacuum system is shown schematically in Figure 2. A brief technical description of the apparatus is presented in the following sections.
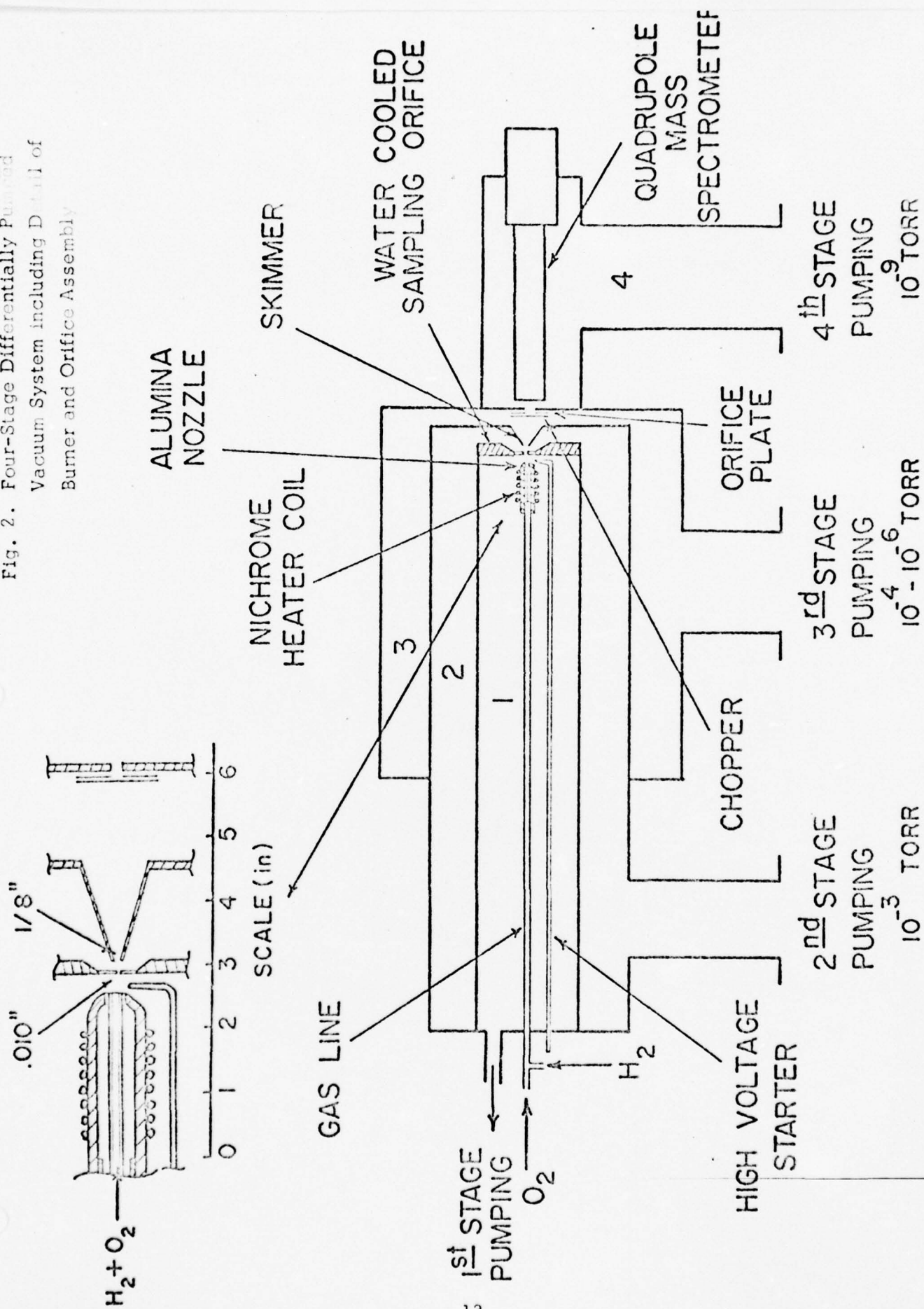
1.   Burner and First Stage

A unique feature of the system is the placement of the sampling orifice to the mass spectrometer inlet (within 3"). The burner was designed as an integral part of the system surrounded by two stages of pumping. In order to facilitate dismantling, modification and realignment of the burner and first two orifices (sampling orifice and molecular beam skimmer) the burner and orifice assembly was con-structed as a demountable portable unit to be attached to the high vacuum pumping stages (which are large fixed facilities). The first stage is

11

MASS (amu)

277 278 279   281
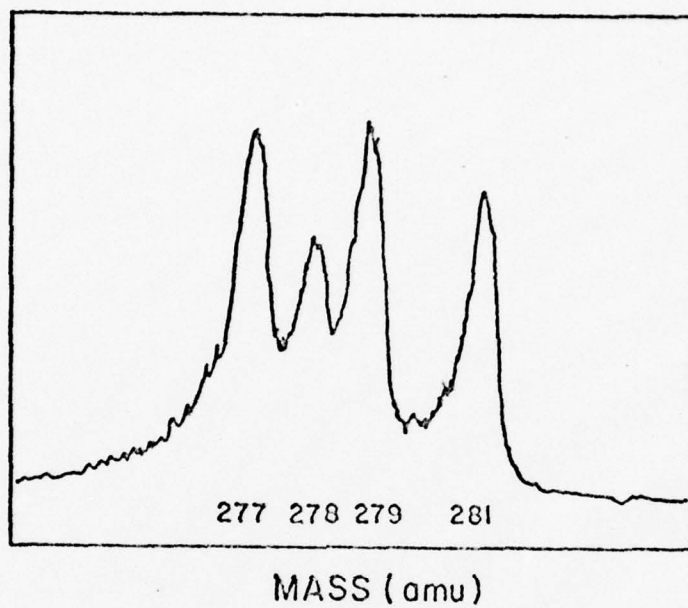
Isotope	Observed Intensity (%)	Analytical Concentration (%)
$W^{180}F_5^+$	–	0.1
$W^{182}F_5^+$	26.3	26.4
$W^{183}F_5^+$	12.8	14.4
$W^{184}F_5^+$	31.6	30.7
$W^{186}F_5^+$	29.3	28.4

Fig. 1. Mass Spectrometer Isotopic Intensities of Major Fragment, WF_5^+, from $WF_6(g)$ (70 eV ionizing energy)

Fig. 2. Four-Stage Differentially Pumped
Vacuum System including Detail of
Burner and Orifice Assembly

ALUMINA
NOZZLE

SKIMMER

WATER COOLED
SAMPLING ORIFICE

NICHROME
HEATER COIL

QUADRUPOLE
MASS
SPECTROMETER

GAS LINE

CHOPPER

ORIFICE
PLATE

4

4ᵗʰ STAGE
PUMPING
10⁻⁹ TORR

3

2

1

3ʳᵈ STAGE
PUMPING
10⁻⁴ - 10⁻⁶ TORR

HIGH VOLTAGE
STARTER

H₂

2ⁿᵈ STAGE
PUMPING
10⁻³ TORR

H₂ + O₂

.010"   1/8"

SCALE (in)

0 1 2 3 4 5 6

1ˢᵗ STAGE
PUMPING

O₂

13

connected to a low capacity vacuum pump to achieve pressures below atmospheric. The first stage vacuum system is fabricated from 3" glass pipe and is mounted inside a 6" i.d. glass pipe T-section which is connected to the second stage of pumping. The flame is ignited by an electric spark and appropriate electrical leads and connections are provided. The burner is surrounded (except for the sight hole) by a copper tube to prevent localized overheating of the glass pipe by the flame. The 12" vacuum chamber (third stage) has a port through which the flame can be observed.

The burner consists of an outer alumina tube 3/8" o.d. by 1/4" i.d. and an inner stainless steel tube 1/16" i.d. through which fuel gas and air are passed. Ceramic orifices, such as alumina, are employed and are heated directly with the flame. The orifice is fitted between two copper plates and water cooled.

2.   Second Stage and Molecular Beam Skimmer

The second stage of pumping consists of a mechanical pump combined with a 6" diffusion pump. The second stage pumping station is connected to the 12" vacuum chamber (third stage) through 6" i.d. glass pipe, which is connected to the 6" T-section mentioned above.

Inside the 12" vacuum chamber the molecular beam skimmer is attached to the cover plate closing the end of the 6" glass pipe. The skimmer is a conical probe located within one mean-free-path of the sampling orifice (mean-free-path of N_2 at 10^{-2} mm is 0.5 cm) for the purpose of conducting a portion of the first expansion jet into a second chamber at a pressure less than 10^{-5} mm. The second orifice is sufficiently large to swallow any shock wave which can otherwise be formed at the cone tip. The skimmer is designed to form a molecular beam representative of the flame gases with a minimum of influence from collisions with surfaces. The skimmer has an exit diameter of 1.0". In addition, the tip of the skimmer cone is made of 0.001" brass foil presenting a very sharp edge to the supersonic gas flow.

3.   Third Stage

a 4" diffusion pump. Inside the vacuum chamber are the aperture plate and the mechanical chopper.

4. Fourth Stage

The fourth stage (also of stainless steel) is attached to the rear of the 12" vacuum chamber and is an integral part of that system. It is evacuated by a mechanical pump and a diffusion pump, nominally of 4" inlet diameter. The third and fourth stages are interconnected through a 3/8" diameter hole.

The mass spectrometer employed in conjunction with this experimental apparatus has been described in the previous section. The method of calculation to obtain species and concentrations from flames have been reported in detail previously.[16]

IV. RESULTS AND DISCUSSION

The mass spectrometer investigation of the organic metallic salts and plateau burning propellants was conducted in three phases. The first phase was a decomposition study of several salts including lead acetate, lead salicylate, lead resorcylate and copper salicylate. In addition, manganese salicylate and silver salicylate were tested. In the second phase lead and copper salicylate were added to an H_2/O_2 flame in the four-stage differentially pumped mass spectrometer apparatus to determine their combustion products. The final phase concerned the investigation of the products of reaction at ignition of two propellants: (1) a double base propellant containing 2.5% lead resorcylate; and (2) a double base propellant containing 2.5% each of copper salicylate and lead resorcylate.

Phase I - Decomposition of Organic Metallic Salts

A. Lead Acetate

The decomposition of lead acetate was studied in a temperature range of 200 to 1300°C. Figures 3 through 7 are typical mass spectrometer samplings depicting decomposition products of the salts. Figure 3 shows the H_2 peak at 410°C. Figure 4 is a scan of the mass range where CH, CH_2, CH_3 and CH_4 would be expected to
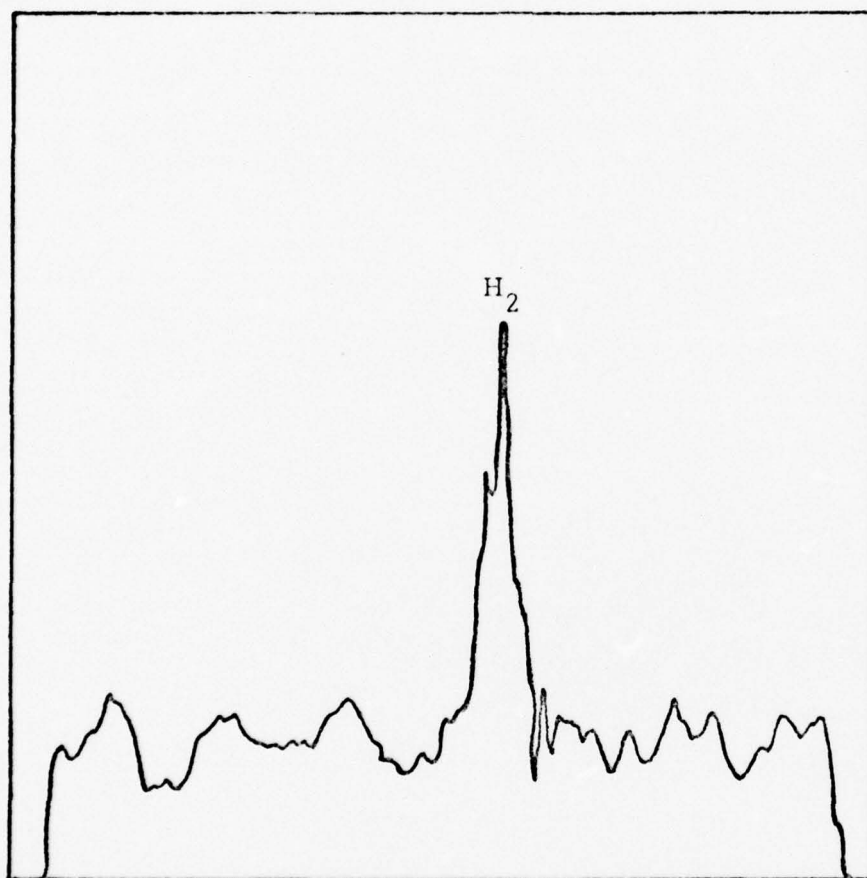
15

Fig. 3. Decomposition of $Pb(C_2H_3O_2)_2$ at $410^{O}C$
(H_2 peak at 2 amu)
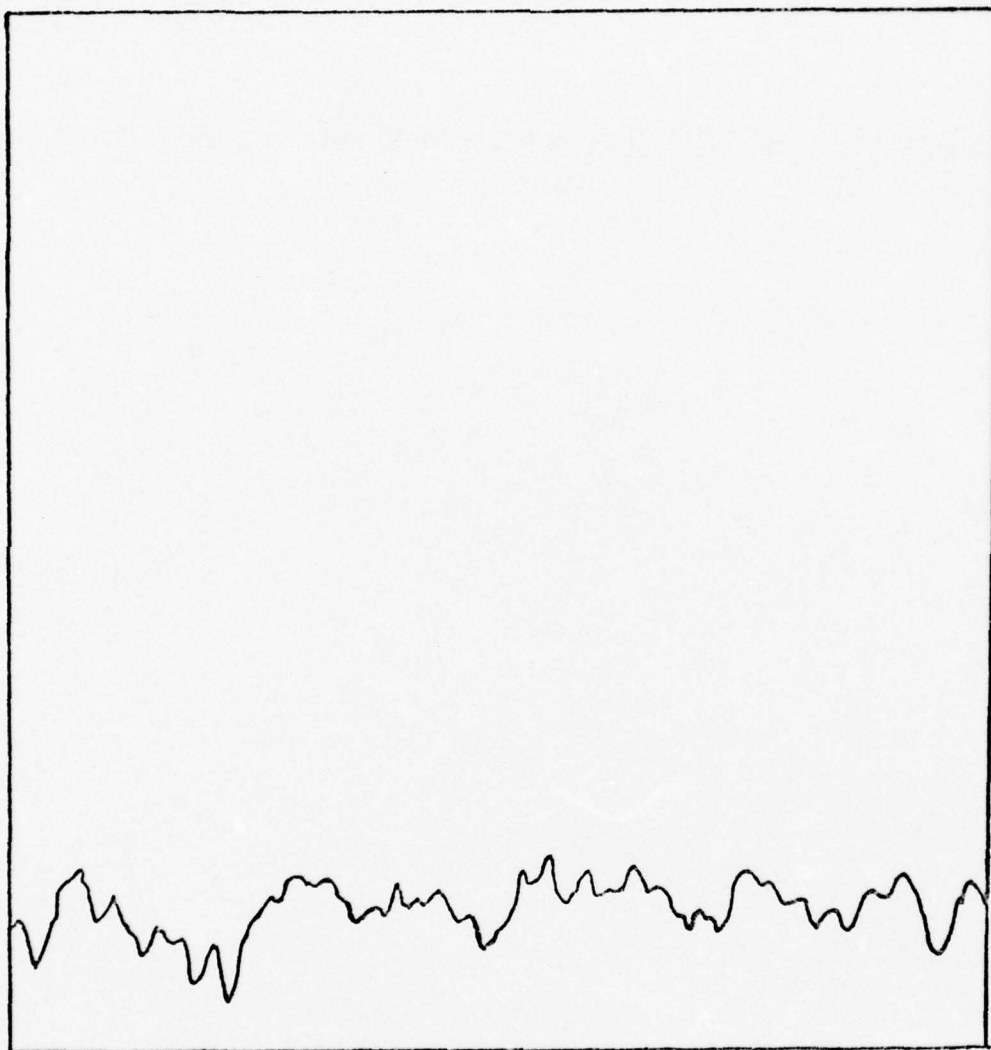
Fig. 4. Decomposition of $Pb(C_2H_3O_2)_2$ at $410^\circ C$
(10 – 16 amu range, no evidence of CH, CH_2, CH_3 or CH_4)
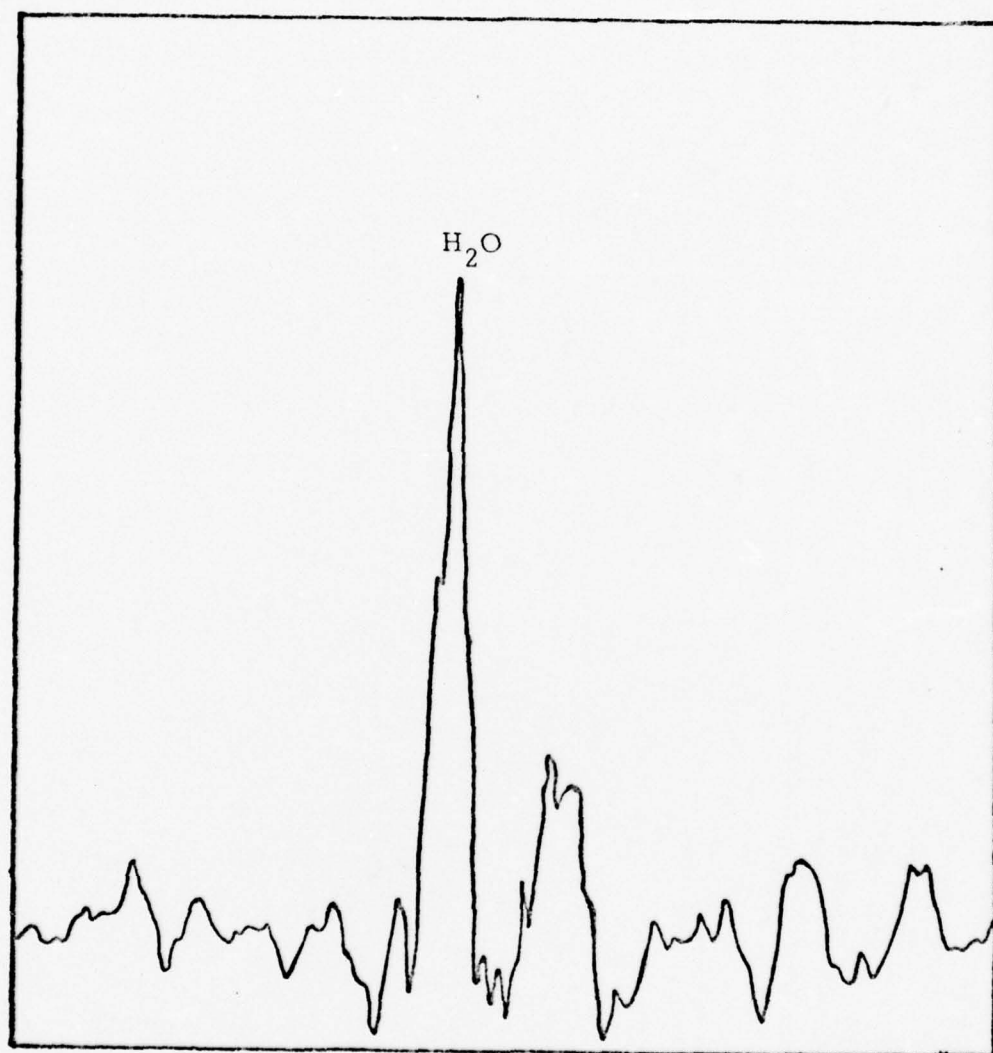
Fig. 5. Decomposition of $Pb(C_2H_3O_2)_2$ at $410^\circ C$
(H_2O peak at 18 amu)

18
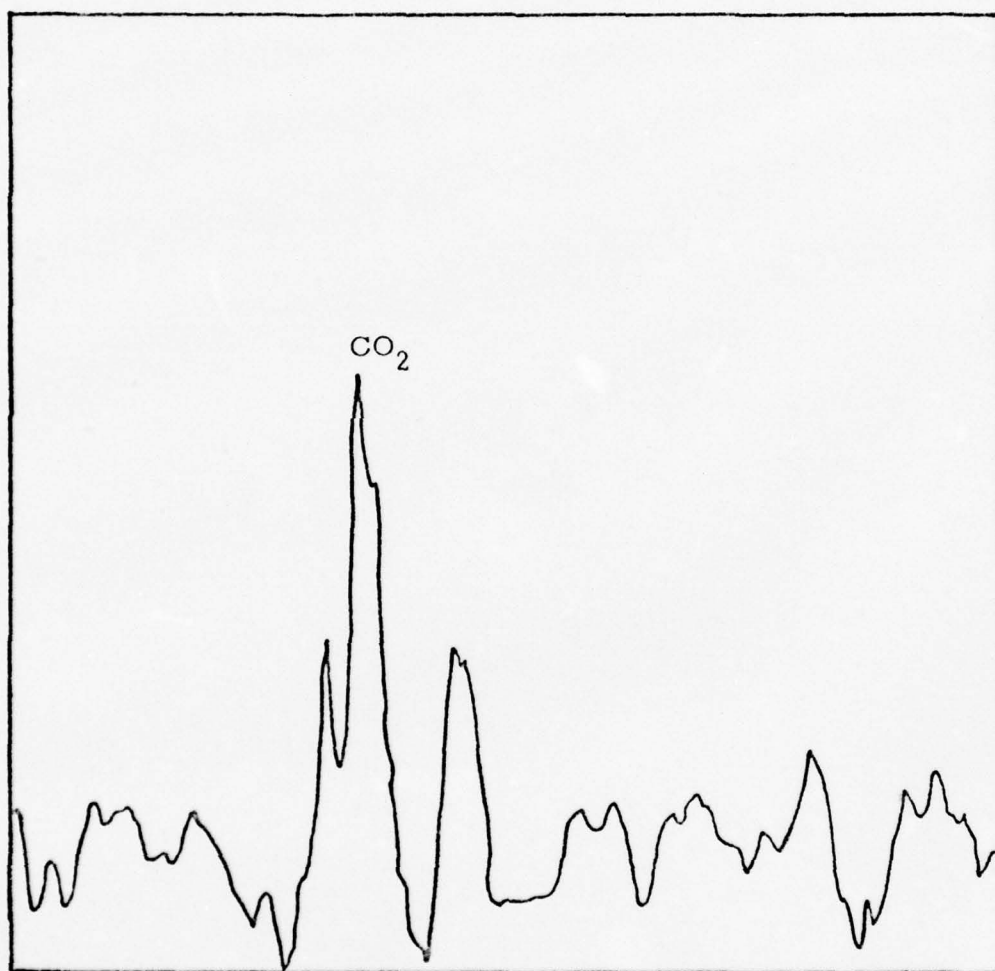
Fig. 6. Decomposition of $Pb(C_2H_3O_2)_2$ at $410^{\circ}C$
(CO_2 peak at 44 amu)
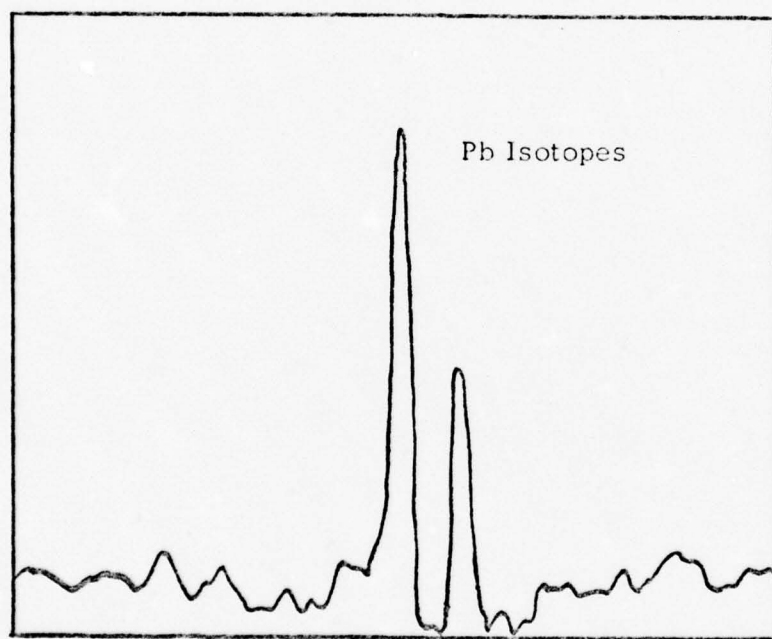
Fig. 7. Decomposition of $Pb(C_2H_3O_2)_2$ at $782^{O}C$

appear; however, none of these species was observed. Figures 5 and 6 depict the H_2O and CO_2 peaks at $410^{\circ}C$. As the organic materials decompose the Pb bonds are broken and the Pb remains in the elemental form, which vaporizes as the temperature increases. Figure 7 shows the Pb isotopes of the vapor at $782^{\circ}C$, with no evidence of PbO or PbO_2. Thus the overall decomposition of the lead acetate in the temperature range of 200 to $1000^{\circ}C$ may be written as

$$
\begin{array}{ccccccc}
H & & O & & O & & H \\
| & & \parallel & & \parallel & & | \\
H-C-&C-&O-&Pb-O-&C-&C-&H \\
| & & & & & & | \\
H & & & & & & H \\
\end{array}
$$

$$\xrightarrow[\text{temp.}]{\text{low}} \quad Pb(s,l) + 2H_2O(g) + H_2(g) + 2CO_2(g) + 2C(s)$$
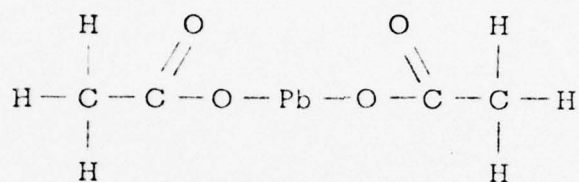
$$\downarrow \text{ high temp.}$$

$$Pb(g) .$$

B.   Lead Salicylate

Similar results were obtained with lead salicylate. However, a benzene peak appeared at low temperatures ($200^{\circ}C$), as shown in Figure 8. A probable mode of decomposition of the salicylate in two temperature ranges (low: 200 to $500^{\circ}C$, and high: 500 to $1000^{\circ}C$) may be written as

$$
\begin{array}{ccccccc}
H & & & & & & H \\
| & & O & & O & & | \\
O & & \parallel & & \parallel & & O \\
\bigcirc-&C-&O-&Pb-&O-&C-&\bigcirc \\
\end{array}
$$

$$\xrightarrow{\text{low temp.}} \quad Pb(s,l) + 2H_2O(g) + 2CO_2(g) + \bigcirc(g) + 6C(s) + 2H_2(g)$$
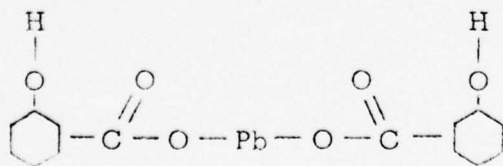
$$\downarrow \qquad\qquad\qquad \text{high temp.} \qquad\qquad \downarrow$$

$$Pb(g) \qquad\qquad\qquad\qquad\qquad\qquad + 3H_2(g)$$

Fig. 8. Benzene Peak at 200°C Appearing from the
Decomposition of $Pb(C_7O_3H_6)_2$

C.   Lead Resorcylate

The results obtained with the decomposition of lead
resorcylate were similar to those obtained with the lead salicylate.
The decomposition follows the path of producing the stable compounds
H_2, H_2O and CO_2, with some benzene appearing at temperatures below
$200^\circ C$. As the temperature is increased the lead atom only appears,
with no evidence of PbO or PbO_2. The possible mode for the overall
decomposition of the lead β-resorcylate may be written as:

low temp.
$$\longrightarrow Pb(s,l) + 2H_2O(g) + 3CO_2(g) + \bigcirc (g) + 5C(s) + H_2(g)$$
$$\downarrow \qquad\qquad \text{high temp.}$$
$$Pb(g) \qquad\qquad\qquad\qquad + 3H_2(g) + 6C(s).$$
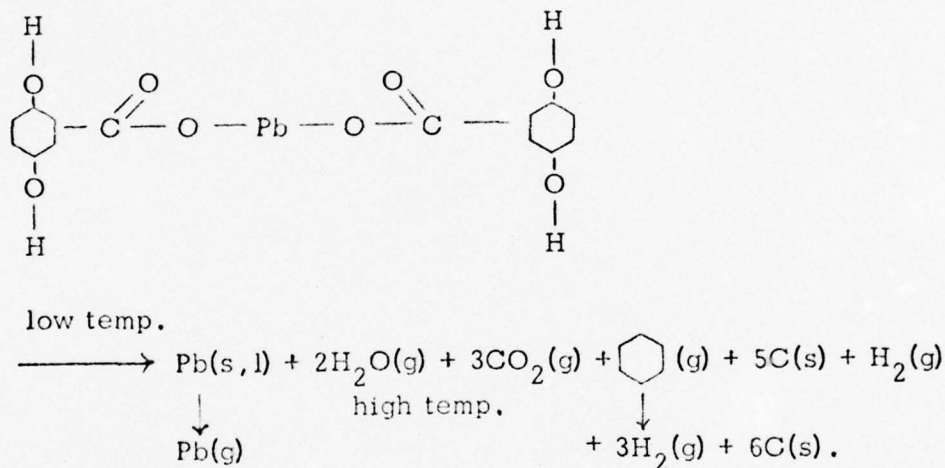
D.   Copper Salicylate

The decomposition study of copper salicylate showed
that, as in the case of the lead salts, the kinetic and thermodynamic
path of decomposition results in the formation of the stable species H_2,
H_2O and CO_2 and gaseous Cu. Representative of the mode of decomposition
are Figures 9 through 12. Figure 9 shows a strong H_2 peak in the 1 to 10
amu range, while Figure 10 depicts a strong H_2O peak in the 10 to 20 amu
range. A strong CO_2 peak appears in Figure 11 in the amu range 40 to 50.
These three typical spectra were taken when the temperature of the cell
containing the copper salicylate reached $500^\circ C$. As in the case of the
lead salicylate, some benzene was noted in the spectrograph. Above $500^\circ C$
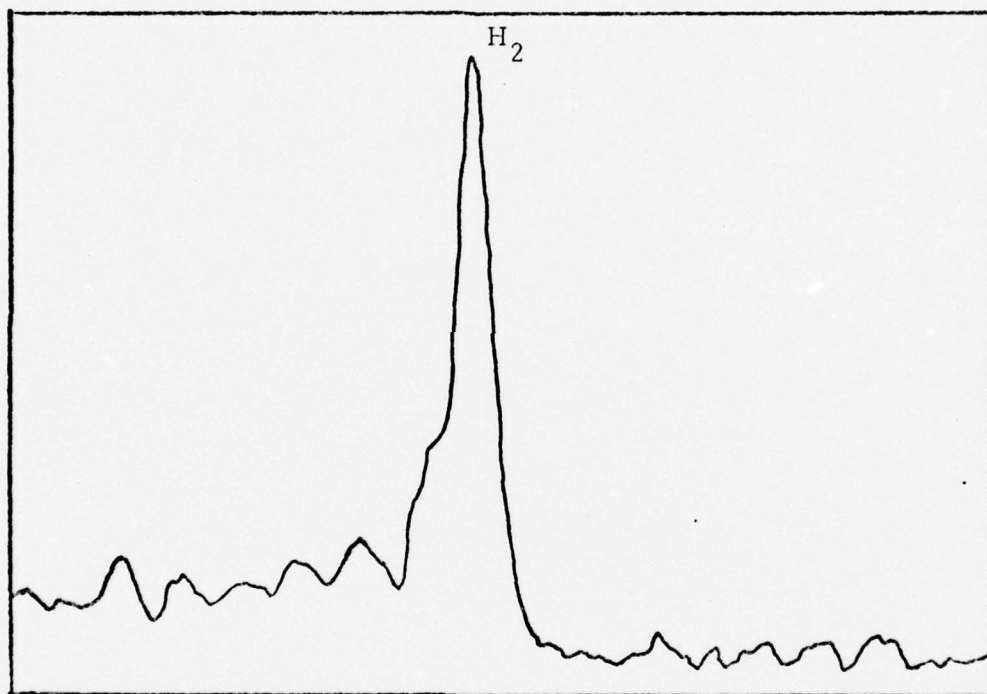no further decomposition products were observed until the metallic copper

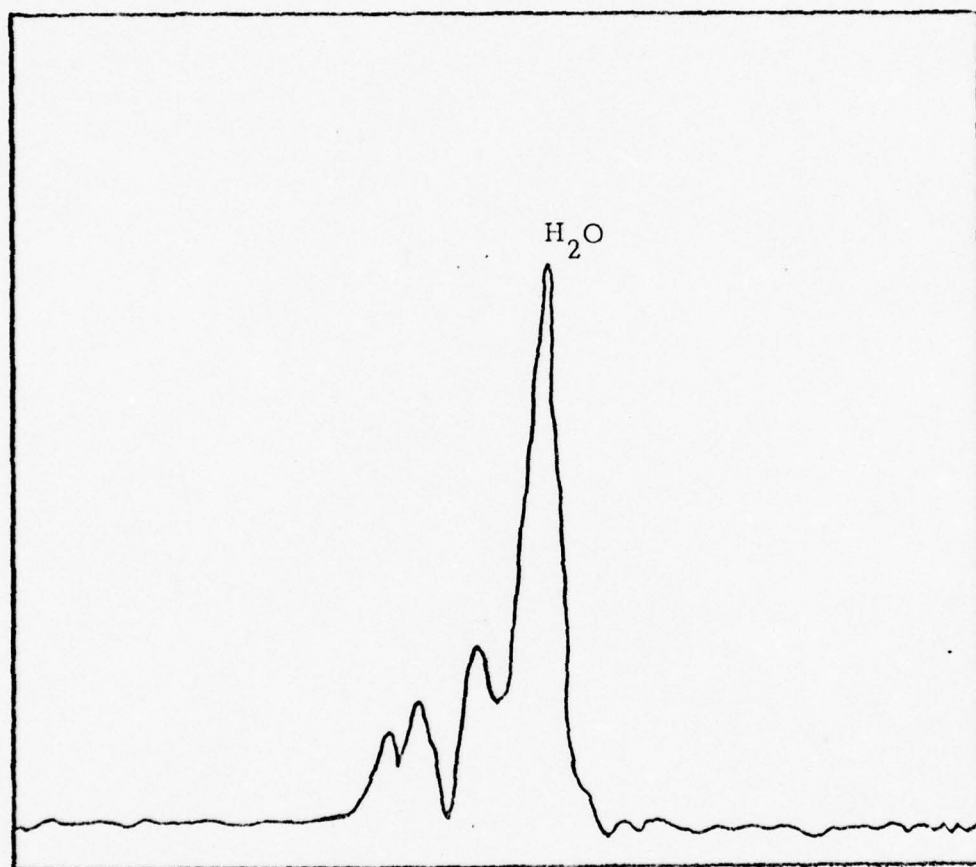Fig. 9. Decomposition of $Cu(C_7H_7O_3)_2$ (H_2 at $500^{\circ}C$)

Fig. 10. Decomposition of $Cu(C_7H_7O_3)_2$ (H_2O at 500^oC)
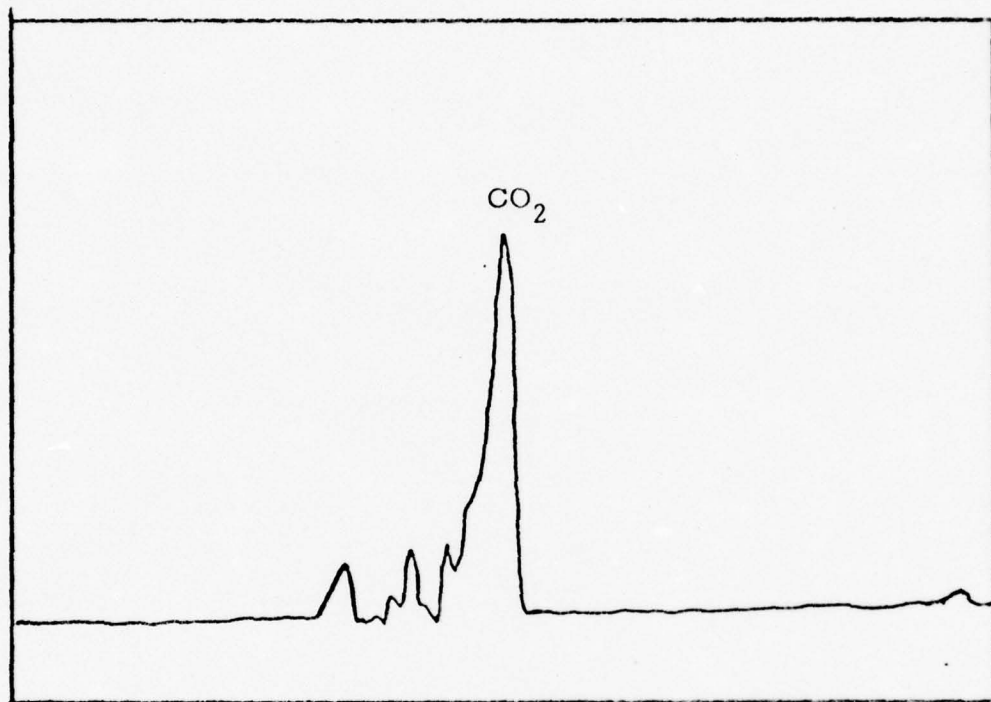
Fig. 11. Decomposition of $Cu(C_7H_7O_3)_2$ (CO_2 at $500^{\circ}C$)
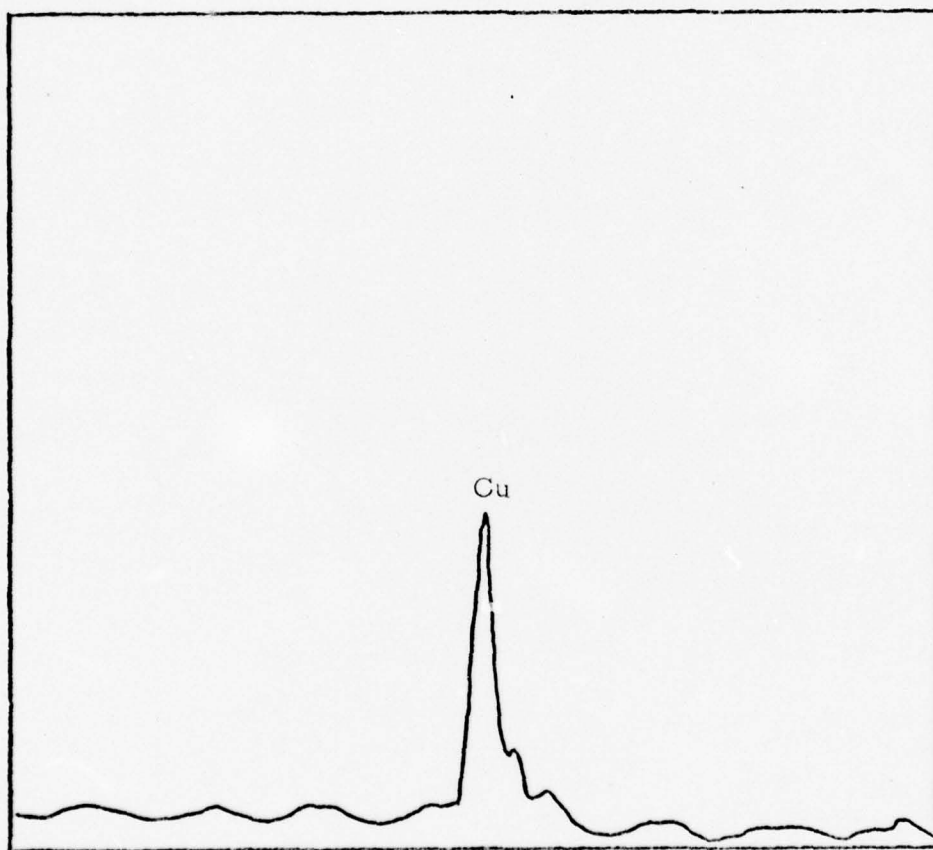
Fig. 12. Decomposition of $Cu(C_7H_7O_3)_2$ (Gaseous Cu Atom at $1370^{\circ}C$)

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began to vaporize. Figure 12 shows a gaseous copper peak at a temperature of 1370°C. The sweep width depicted in this figure is 70 amu, i.e., 35 amu on each side of the Cu atom at 63 amu. No CuO(g) is seen at amu 79. The free energy for the reaction of Cu and H_2O

$$Cu(g) + H_2O(g) = CuO(g) + H_2(g)$$
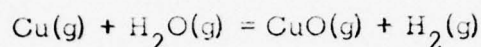
at 1600°K is +28.8 kcal/mole. Thus the reaction to form gaseous CuO would not be thermodynamically feasible; however, it is likely that the condensed phase of CuO(c) may occur. The probable mechanism for the thermal degradation of the copper salicylate is

low
temp.
$$\longrightarrow Cu(s) + 2H_2O(g) + 2CO_2(g) + \bigcirc(g) + 6C(s) + 2H_2(g)$$

$$\downarrow \qquad \text{high temp.} \qquad \downarrow$$

$$Cu(g) \qquad\qquad\qquad\qquad + 3H_2(g) + 6C(s).$$
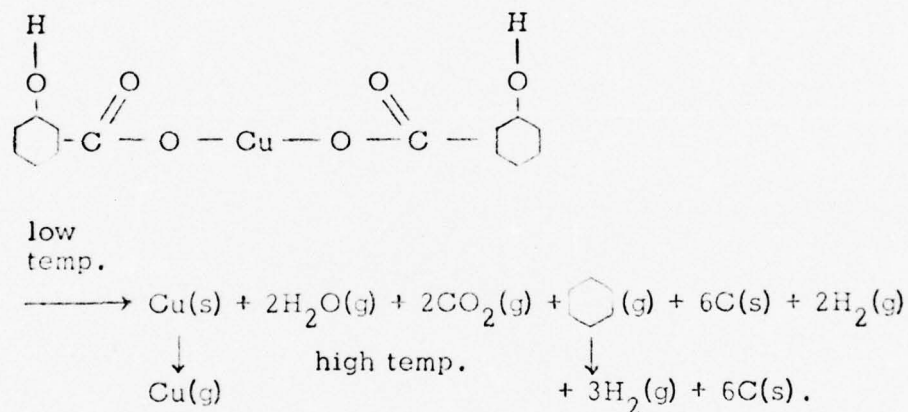
E.   Silver and Manganese Salicylate

The decomposition pattern of organic salts of manganese and silver was also studied although they have not been successfully employed as plateau burning catalysts. The decomposition of silver salicylate followed the path of the lead and copper salts. However, in addition to metallic silver atoms, a small amount of AgO was seen in the mass spectrometer tracing at a temperature of 1200°K (Figure 13). Pyrolysis of manganese salicylate produced MnO, however, in quantities nearly equal to those of the Mn element. Figure 14 shows the decomposition spectra of manganese salicylate at 1500°K. Neglecting the kinetics,
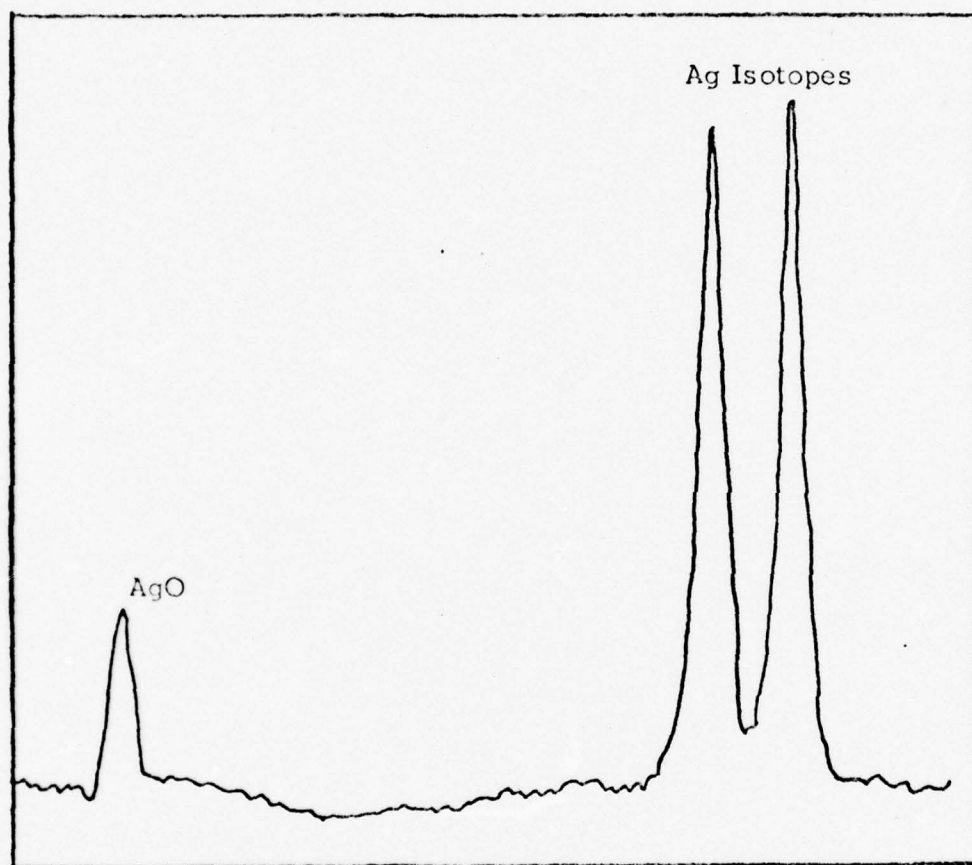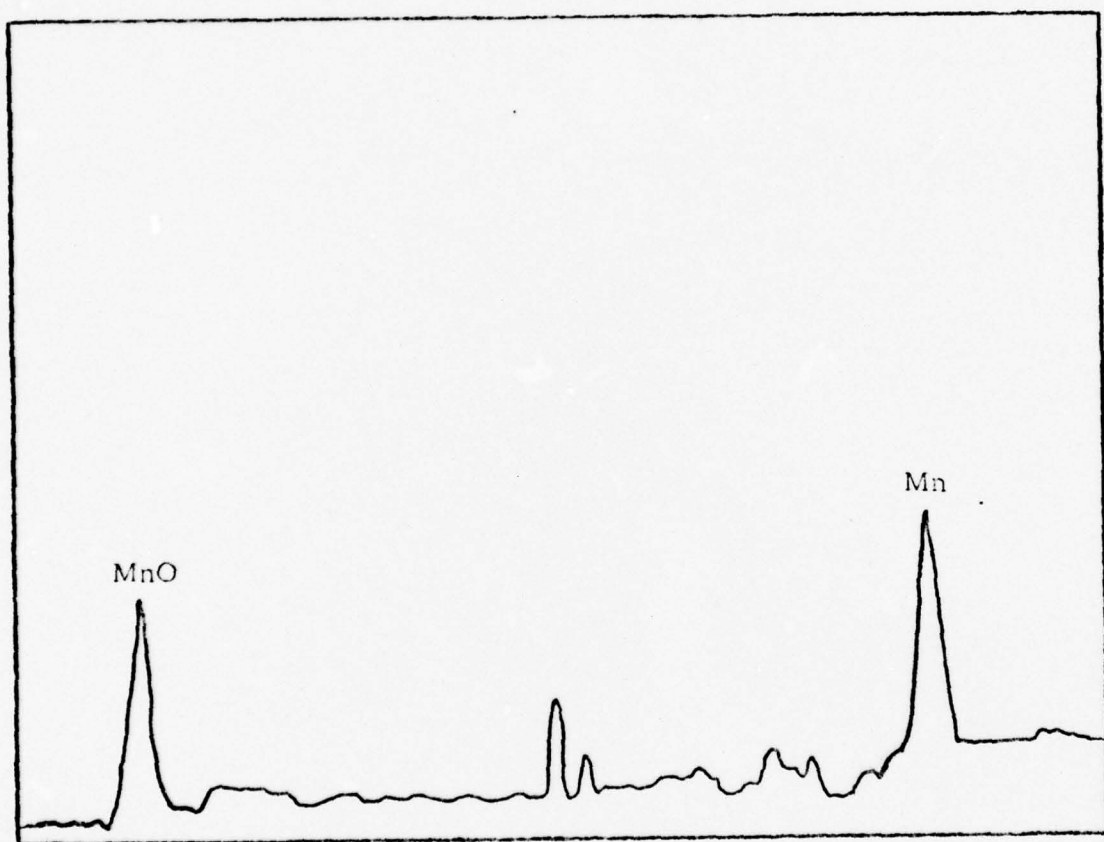
Fig. 13. Decomposition of $Ag(C_7H_7O_3)_2$ at $1200^O K$

Fig. 14. Decomposition of $Mn(C_7H_7O_3)_2$ at $1500\,^{\circ}K$

and based only on thermodynamic considerations, it would be expected that the stability of MnO(g) would be greater than that of AgO(g). Brewer[17] lists the dissociation energy of AgO as 32 kcal/mole and of MnO as 95 kcal/mole.

Although the decomposition of the salicylates is chiefly kinetic, they are temperature dependent. A study was made concerning the rate of evolution of H_2O from manganese salicylate in the temperature range 200 to 300°C over a 30-minute period (see Figure 15). As can be seen, during this period the evolution of H_2O increased nearly two-fold with the rise in temperature. The H_2O concentration decreased during the last half of the period as the sample became depleted.

The pyrolysis and decomposition studies have yielded the important result that the lead and copper atoms are freed from their organic compound at temperatures well below the combustion range. Thus these metallic elements are able to react with the nitrate esters in the pre-combustion zone.

Phase II - Combustion Studies of Lead and Copper Additives

This laboratory's four-stage differentially pumped molecular beam mass spectrometer apparatus described in Section III was employed to study the combustion products of lead and copper additives.

A.   Lead Salicylate

Although the low temperature decomposition and pyrolysis studies showed the gaseous Pb atoms available for reaction with the nitrate esters, their higher temperature combustion showed the Pb reacting in thermochemical equilibrium. Figure 16 shows the major peaks found during the combustion of lead salicylate at 2300°K. There were Pb, PbO, PbO_2 and H_3PbO_4 in nearly equal concentrations. From the reaction thermodynamics free energies were calculated for these species.

For the reaction

$$Pb(g) + H_2O(g) = PbO(g) + H_2(g)$$
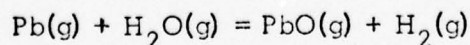
a ΔG of 15.3 kcal/mole was obtained. This results in a ΔH_{f298} value of 12 ± 5 kcal/mole for PbO, which is in fairly good agreement with
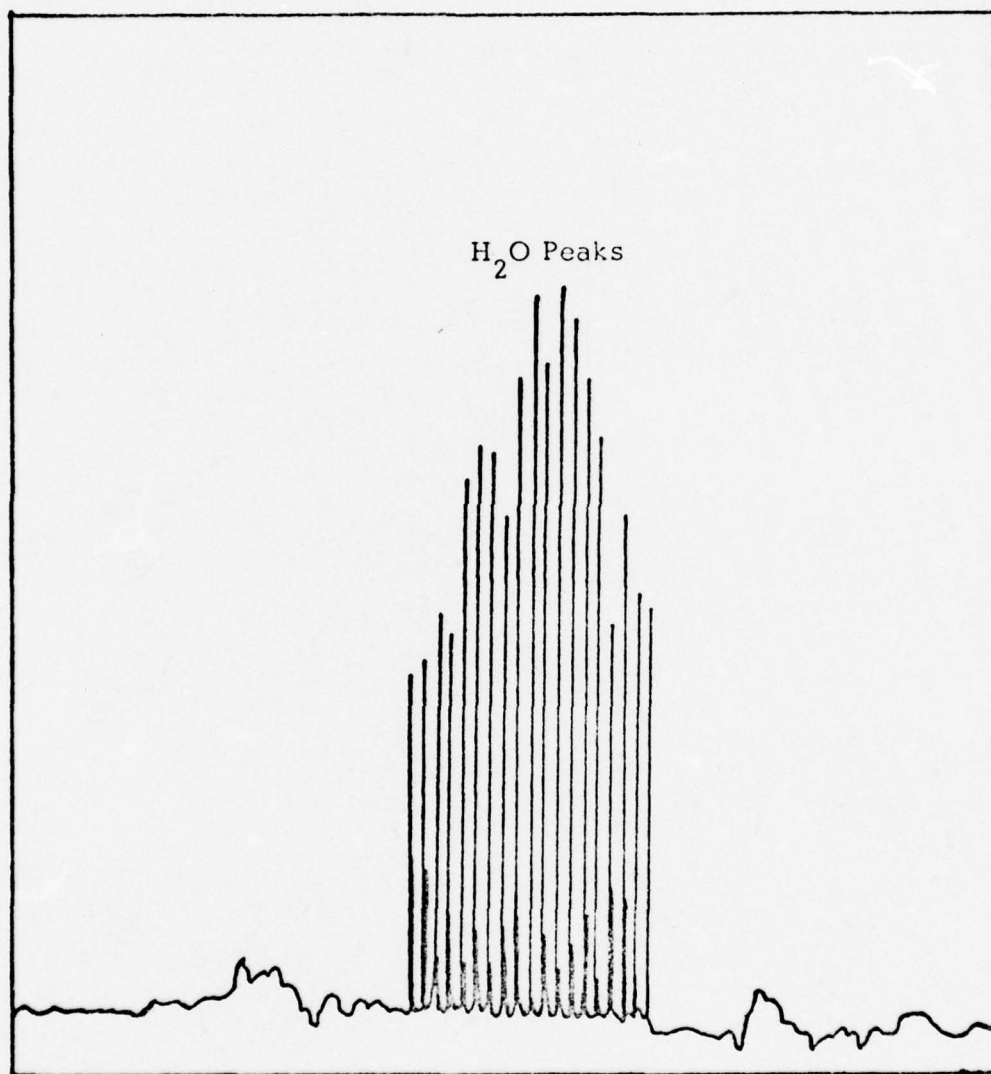
31

Fig. 15. Rate of Evolution of H_2O from Mn Salicylate at 200°C for a Thirty-Minute Interval

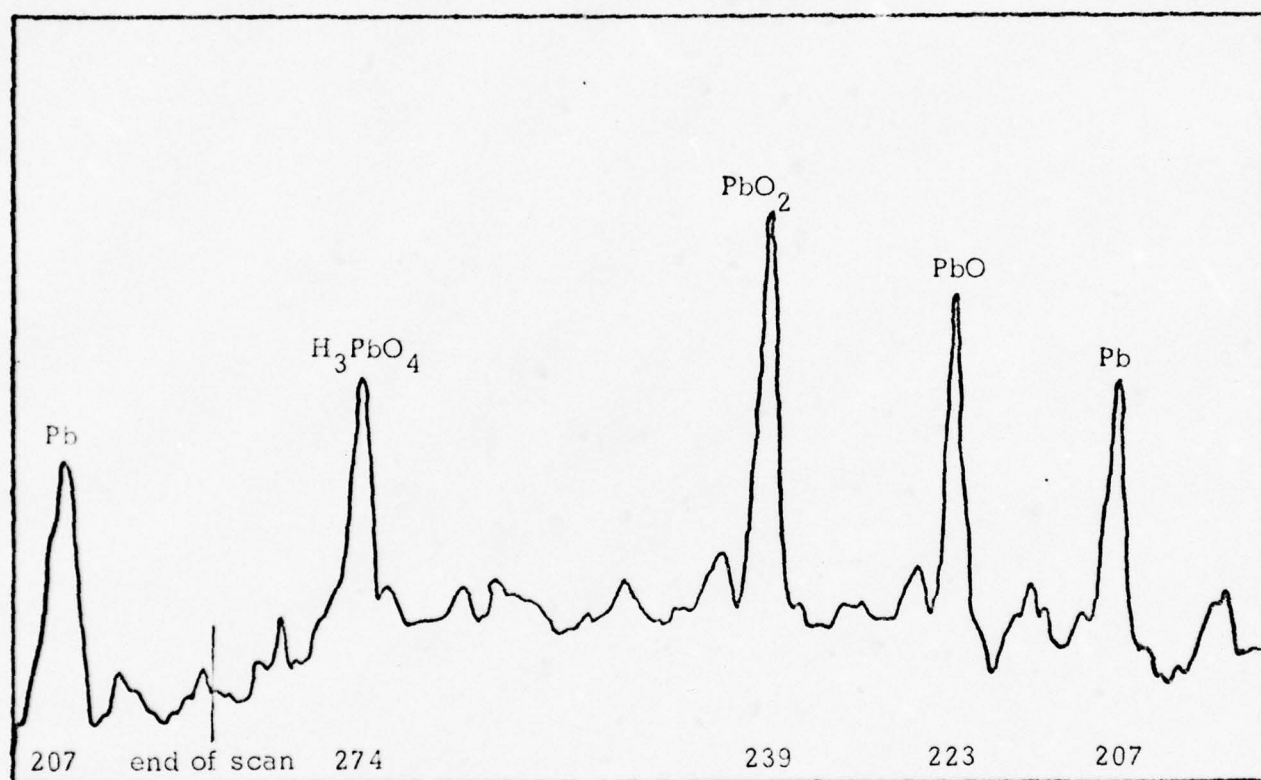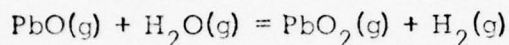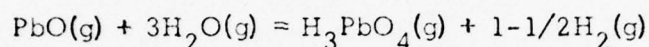Fig. 16. Pb Salicylate at 2300°K in the H_2/O_2 Flame

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the value of 16 kcal/mole reported in the JANAF Tables.[18]

For the reaction

$$PbO(g) + H_2O(g) = PbO_2(g) + H_2(g)$$

a $\triangle G$ of 16.5 kcal/mole is obtained. This results in a $\triangle H_{f298}$ value of -24.5 ± 5 kcal/mole for $PbO_2(g)$.

For the reaction

$$PbO(g) + 3H_2O(g) = H_3PbO_4(g) + 1-1/2H_2(g)$$

a $\triangle G$ of 35.2 kcal/mole is obtained at $2350^\circ K$. This results in a $\triangle H_{f298}$ of -62.3 kcal/mole for $H_3PbO_4(g)$.

The reaction enthalpies would indicate that the final combustion products of the lead additives are those predicted by their thermodynamic equilibrium. Thus it appears that the intermediates are responsible for the plateau.

B. Copper Salicylate

As in the case of the lead salicylate, high temperature combustion (at $2300^\circ K$) of copper salicylate shows the formation of cupric oxide and cupric hydroxide in nearly equal concentrations, as can be seen from Figure 17. Free energies can be calculated for the reactions. A $\triangle G$ of 27.4 kcal/mole is calculated for the reaction

$$Cu(g) + H_2O(g) = CuO(g) + H_2(g).$$
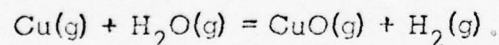
A $\triangle G$ of 0 is calculated for the reaction

$$CuO(g) + H_2O(g) = Cu(OH)_2(g).$$
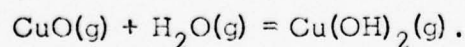
Phase III - Investigation of Ignition Products of Plateau Burning Propellants

The mass spectrometer techniques described in the previous section were employed to study the reaction products of the plateau burning propellants at ignition. The propellant sample was placed in an effusion cell which
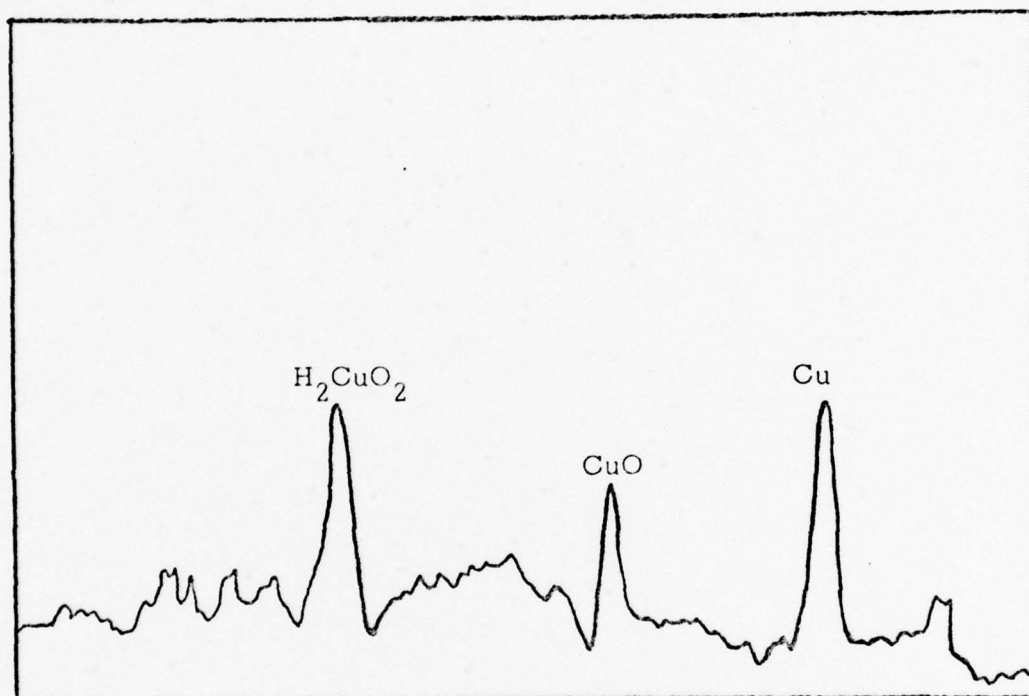
34

Fig. 17. Cu Salicylate at 2300°K in the H_2/O_2 Flame

was heated gradually until ignition occurred. The amu range was monitored continuously in order to receive any species arriving from the ignition of the sample. The time-of-flight of a species within the quadrupole section is in the microsecond range. Thus the initial products formed in the propellant reaction can be identified. Also, intermediate species having a short lifetime (on the order of milliseconds) would be receivable at the mass spectrometer.

The plateau burning propellants investigated were N-5, containing 2.5% lead resorcylate, and HEX-12, containing 2.5% each of copper salicylate and lead resorcylate. An ordinary double base propellant, JPN, was also studied for comparison of the products of reaction.

A. Ordinary Double Base Propellant

The JPN propellant studies were made near the ignition temperature, approximately $200^{\circ}C$, to determine the first species arriving at the mass spectrometer as a result of ignition. The propellant was contained in a heated effusion cell and the vapor species produced at the point of ignition were determined at fixed settings on the mass spectrometer. Figure 18 shows H_2 coming off the cell temperature of $180^{\circ}C$, while Figure 19 shows N_2, CO, NO and O_2 peaks at the same temperature. As can be seen from Figure 20, very strong CO_2 and NO_2 peaks are produced. Considerable amounts of H_2O are also present. From these mass spectrometer ignition studies it appears that the decomposition of double base propellants follows the classical pattern, producing H_2, H_2O, N_2, NO, CO_2 and NO_2.

Following the ignition studies the combustion products of JPN were examined. Figure 21 shows these species to be H_2O, N_2, and CO_2, with a small quantity of NO. The NO_2 concentration was negligible. Thus the mode of decomposition follows the initial break-up of the nitrate ester into NO and NO_2 groups, with a considerable quantity of molecular hydrogen; the subsequent combustion follows the equilibrium mode, producing the major species as predicted by the thermodynamic equilibria.

B. Lead Additive Double Base Propellant

For the investigation of the plateau burning propellant N-5 the mass spectrometer was set to receive species in the atomic mass
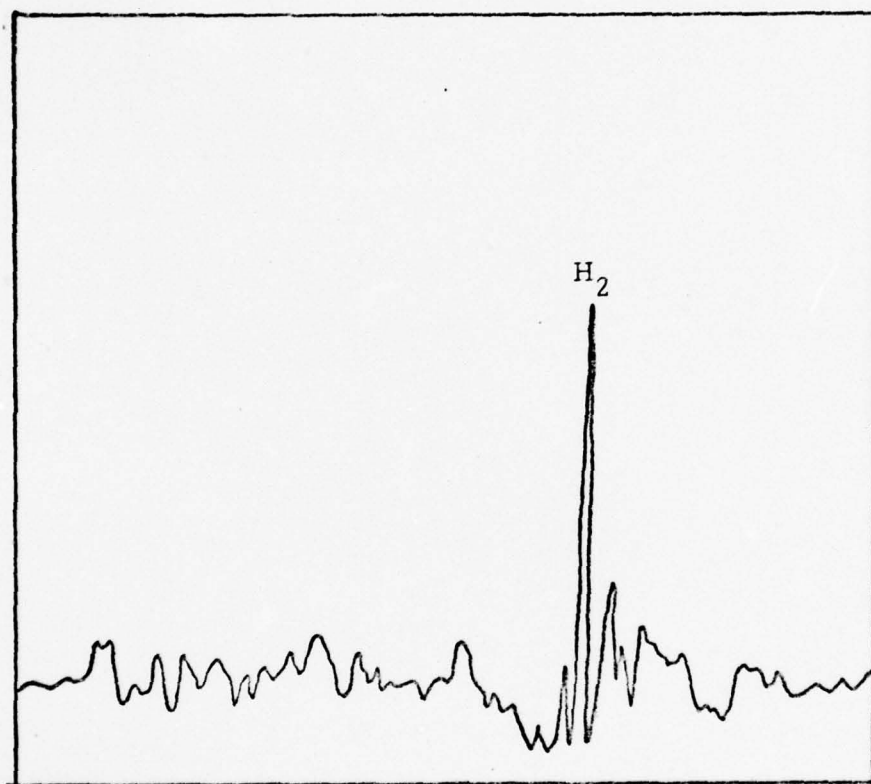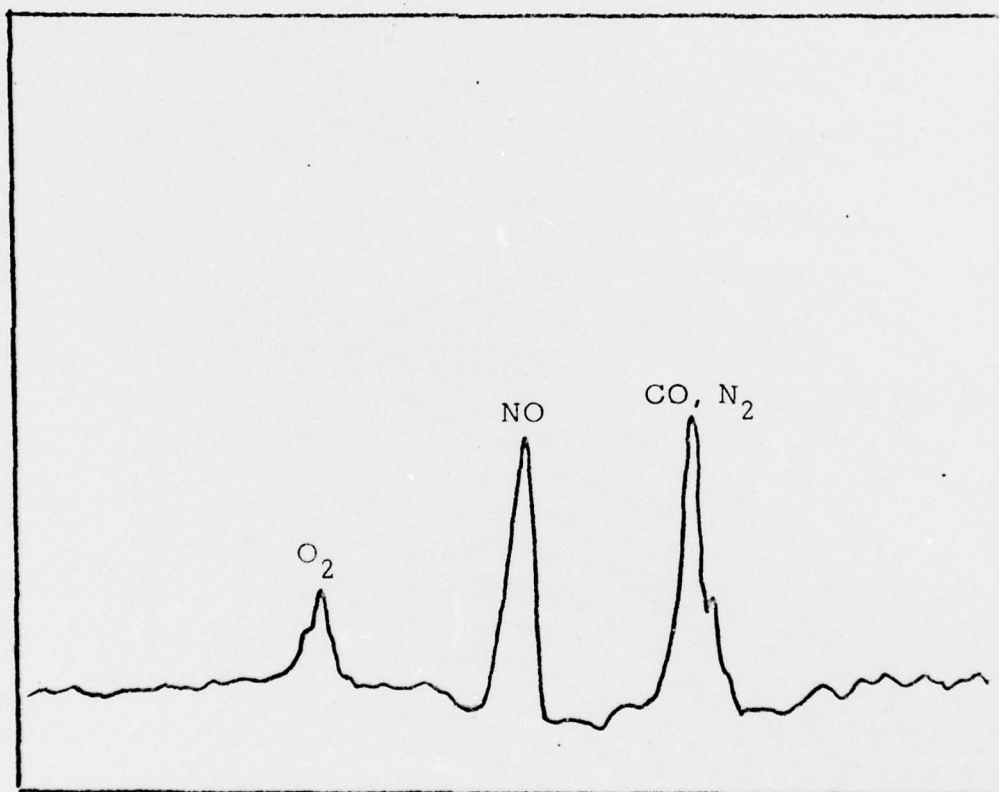
Fig. 18. Decomposition of JPN Propellant

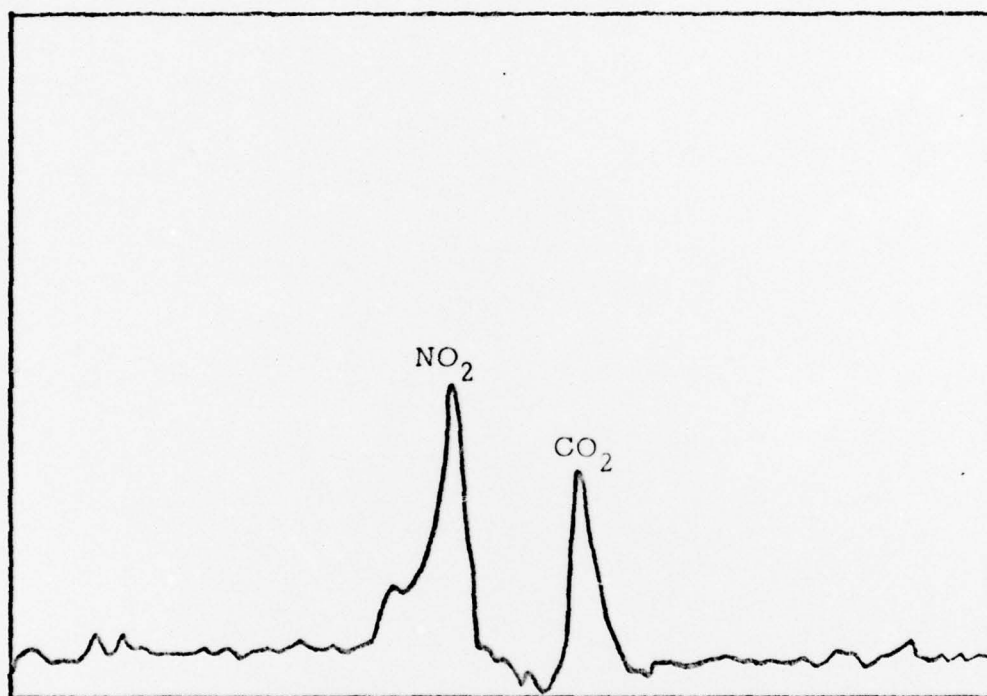Fig. 19. Decomposition of JPN Propellant
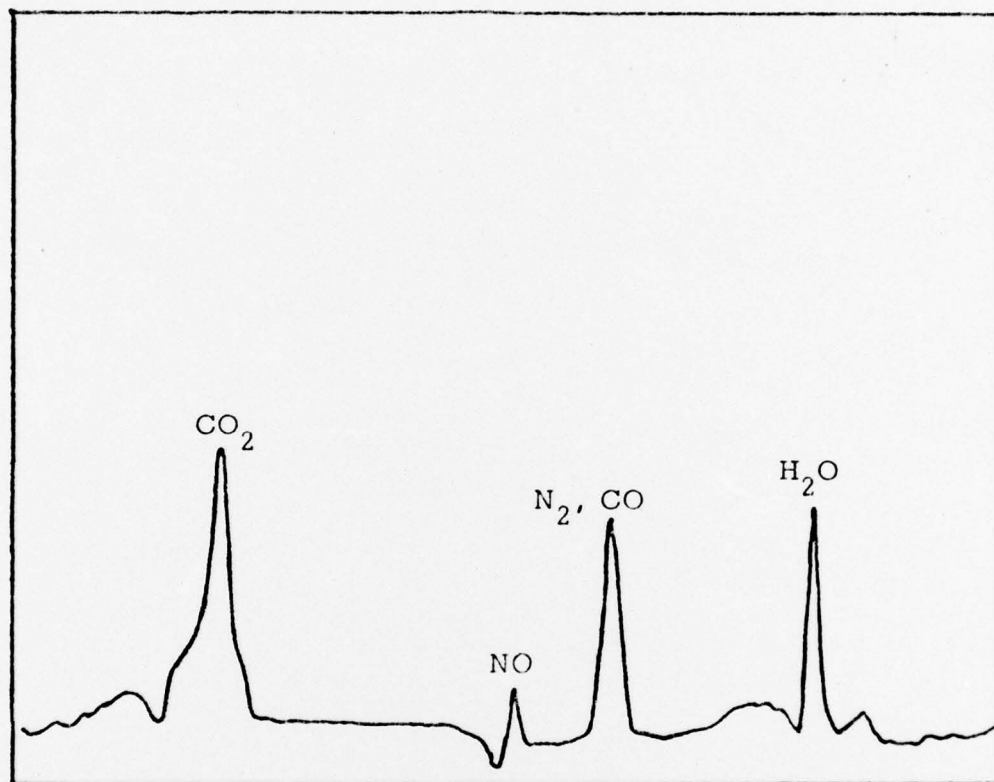
Fig. 20. JPN Propellant at Ignition

Fig. 21. Major Flame Species of JPN Propellant

range of 200 to 300, which would include Pb intermediates or compounds. The effusion cell was gradually heated until a pressure change was noted on the ionization gauge, indicating a release of gaseous material. After ignition, but prior to combustion, gaseous atomic Pb and $PbNO_2$ were observed in the mass spectrometer. Figure 22 shows the noise level in the 200 - 300 amu range as the cell was being heated. Figure 23 shows the Pb and $PbNO_2$ arriving at the mass spectrometer after ignition occurred.

The formation of $PbNO_2$ as an intermediate results from the breakdown of the nitrate esters into NO_2 groups which are readily attached to the gaseous Pb atoms. The free energy of reaction would favor this type of compound formation. Other N-5 propellant species produced were also identified. Figures 24 through 26 show the major vapor species present after ignition. Figure 24 covers the mass range from 15 to 18, showing H_2O, OH and CH_3 peaks. Figure 25 depicts the range 24 to 32, with C_2H_2, CO, N_2, NO and O_2 peaks appearing. Figure 26 covers the 44 to 46 mass range, showing CO_2 and NO_2 peaks. These data indicate that at ignition and prior to reaching the adiabatic combustion temperature, hydrocarbons and NO_2 are produced. The gaseous Pb atoms can combine with the NO_2 and form $PbNO_2$, thereby holding some of the nitrite without further reaction in the intermediate phase prior to steady state combustion.

C.   Copper and Lead Additive Double Base Propellant

Following studies of the N-5 propellant the HEX-12 propellant containing approximately 2.5% each of lead β-resorcylate and cupric salicylate was examined.

Initially, ignition studies were conducted, with the mass spectrometer set to cover the amu range 60 to 130 to determine the species Cu, CuO, CuOH, CuNO, $CuNO_2$ and $CuNO_3$, if present at ignition. The propellant was heated gradually in an effusion cell until ignition occurred. Repeated runs were made at the various amu peaks to determine whether any Cu species were present.

Figure 27 shows a good peak of Cu(g) species at ignition. Figure 28 is a composite oscilloscope tracing showing the mass spectrometer functioning before and after ignition. As can be seen from Figure 28, no
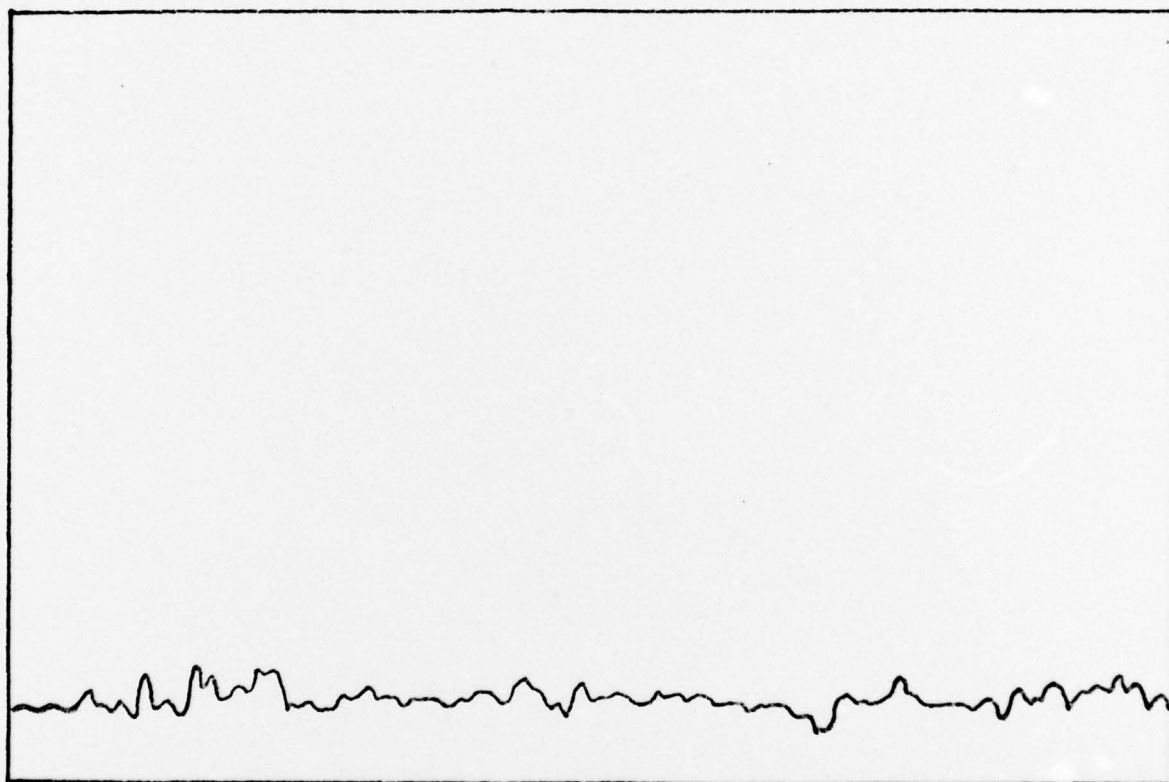
41

Fig. 22. Mass Spectrum of N-5 Propellant in the 200 - 275 amu Range
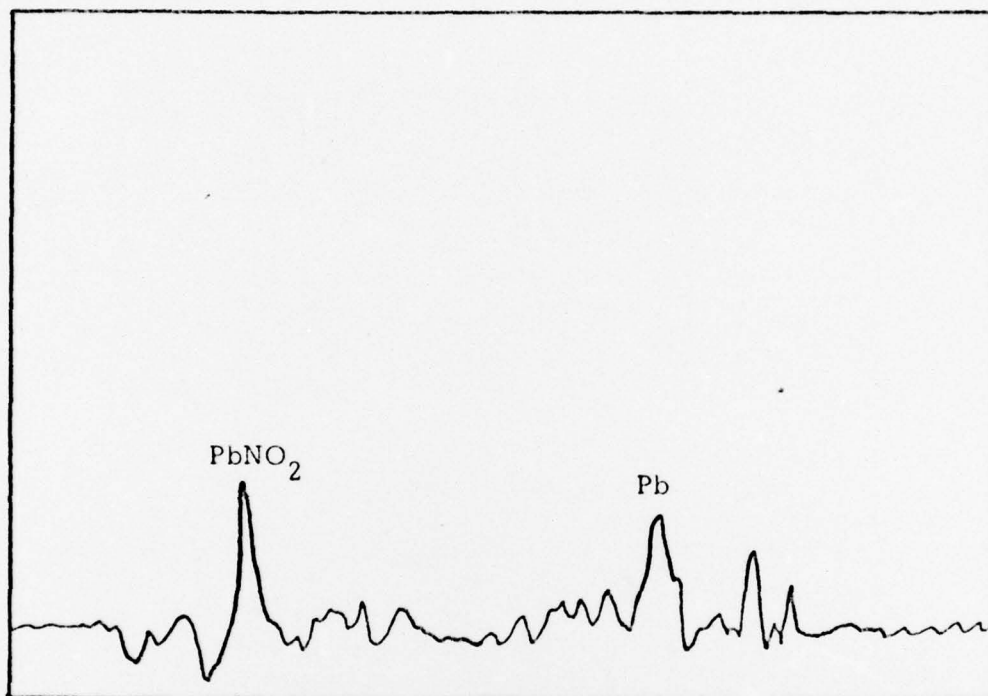Prior to Ignition

Fig. 23. Mass Spectrum of N-5 Propellant in the 200 - 275
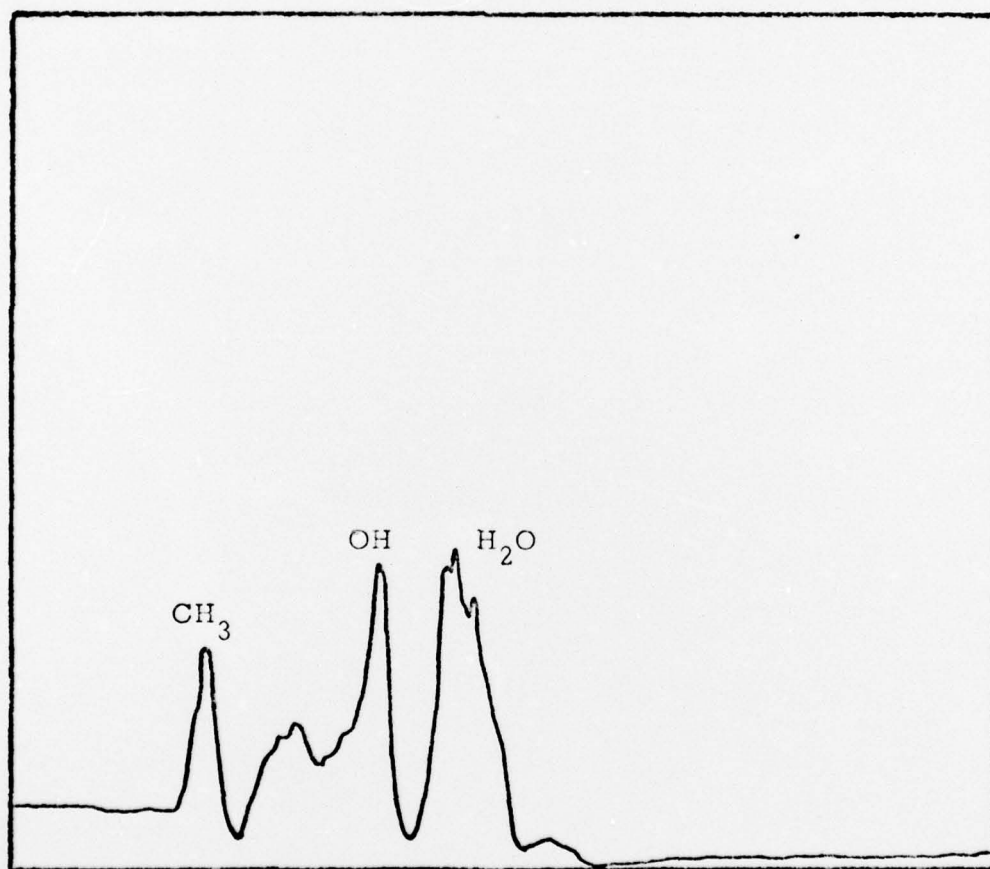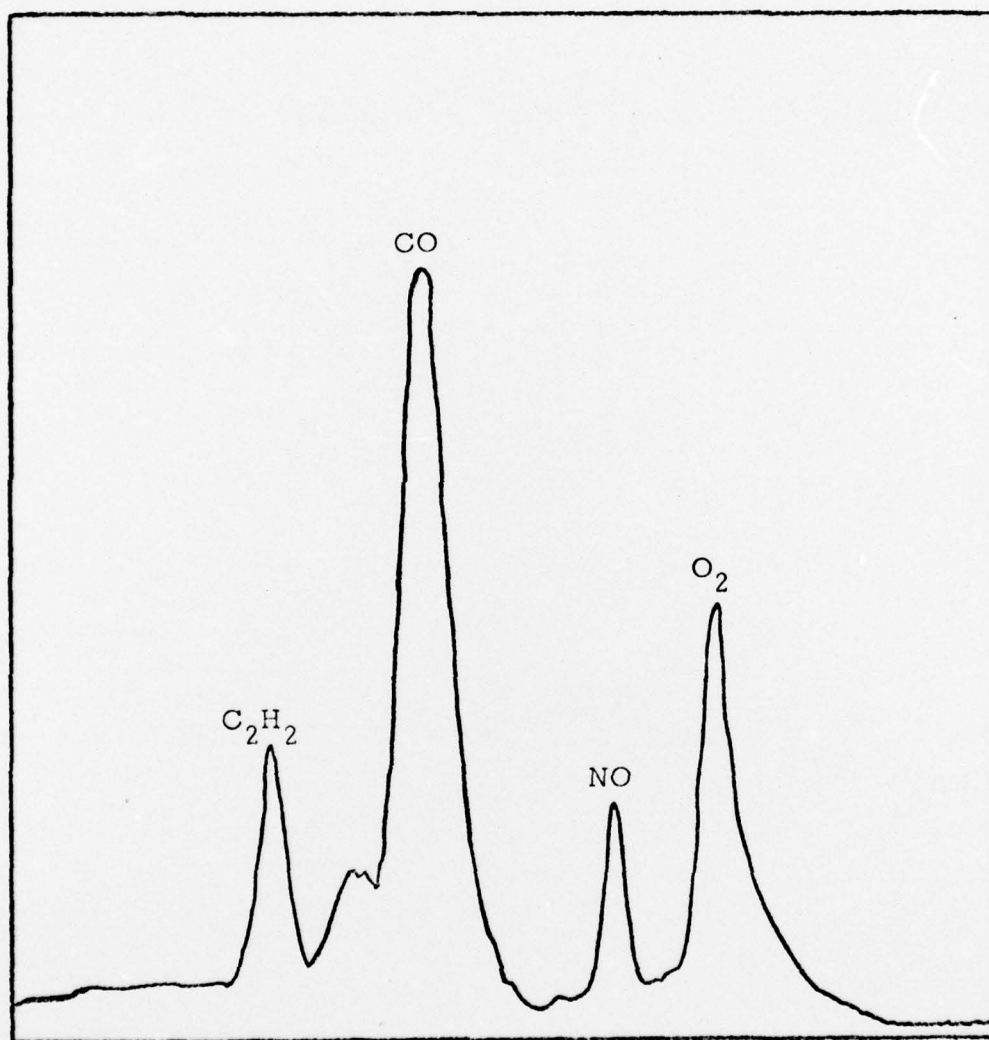amu Range at Ignition

Fig. 24. N-5 Propellant at Ignition

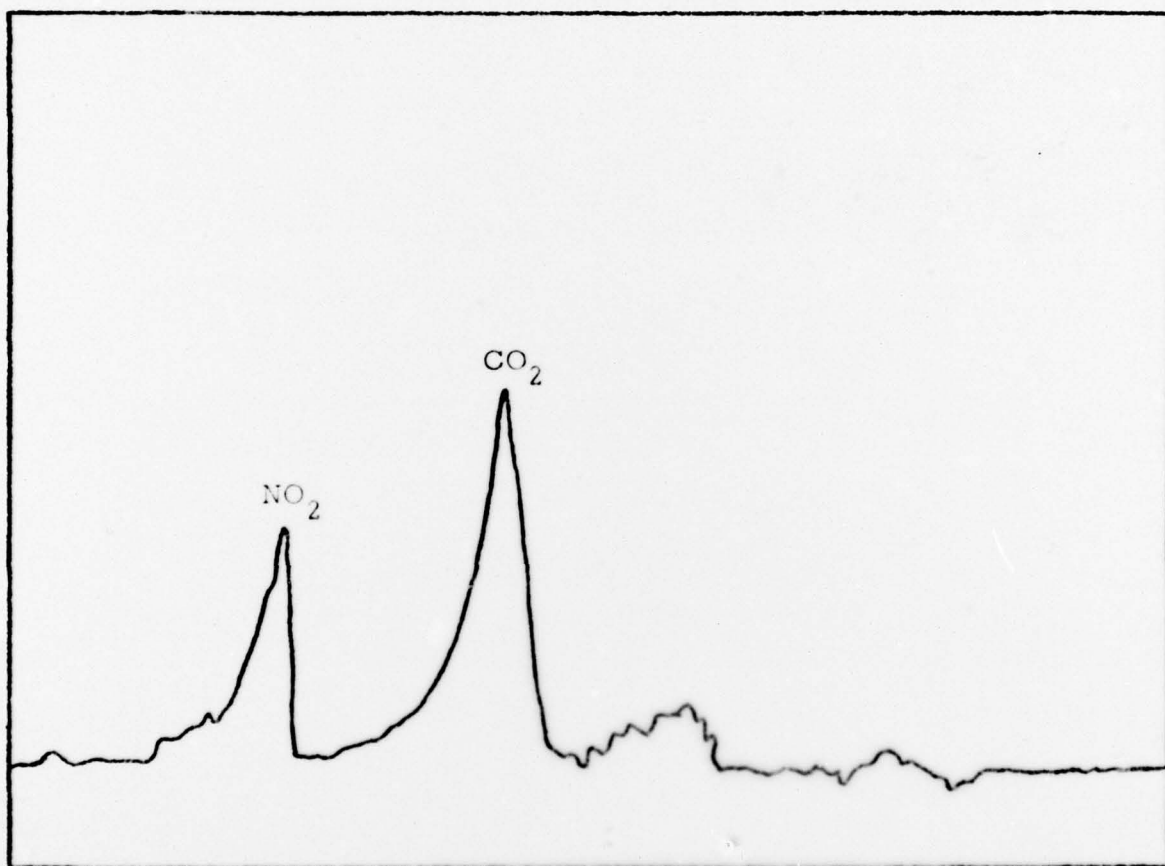Fig. 25. N-5 Propellant at Ignition

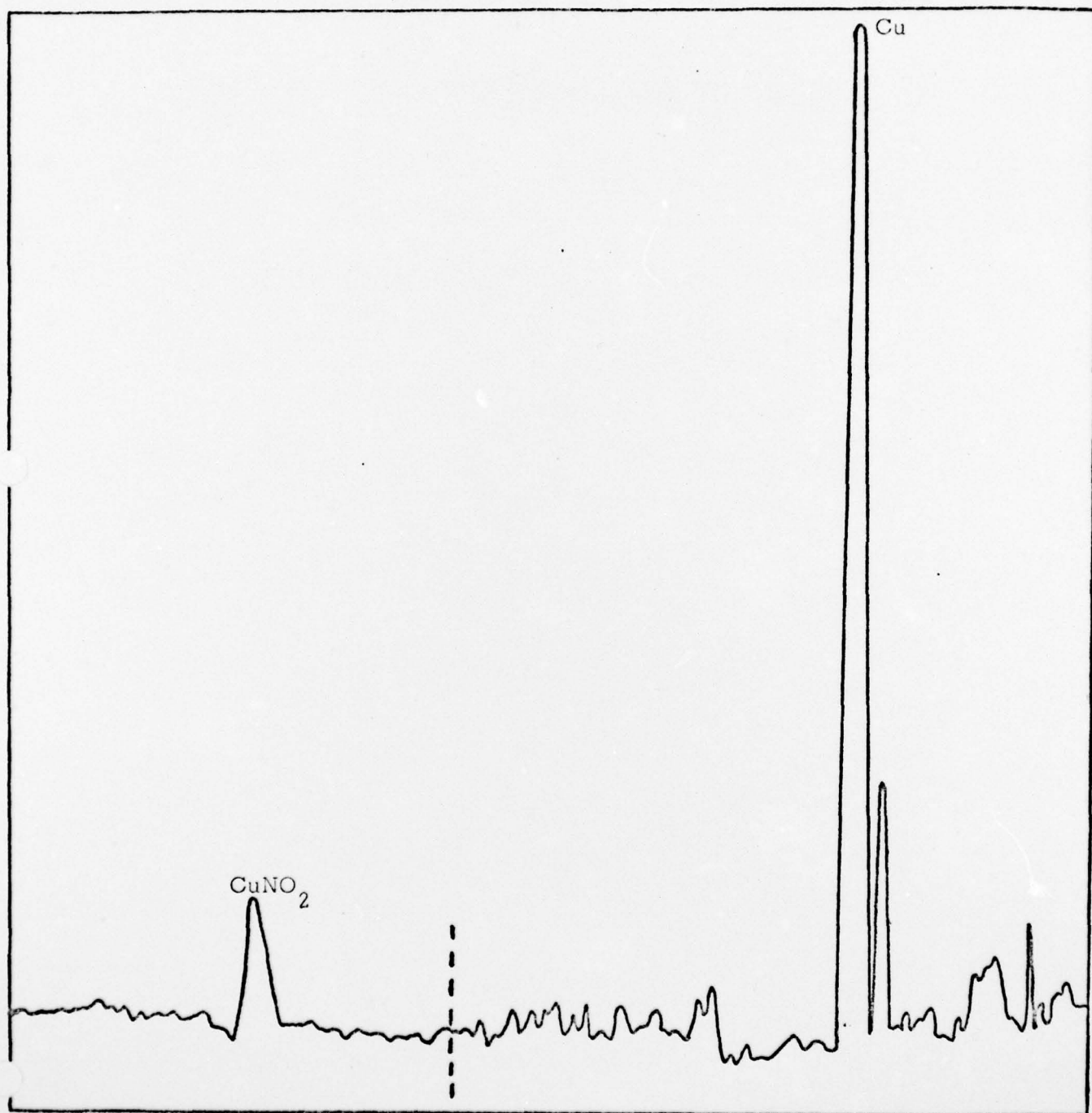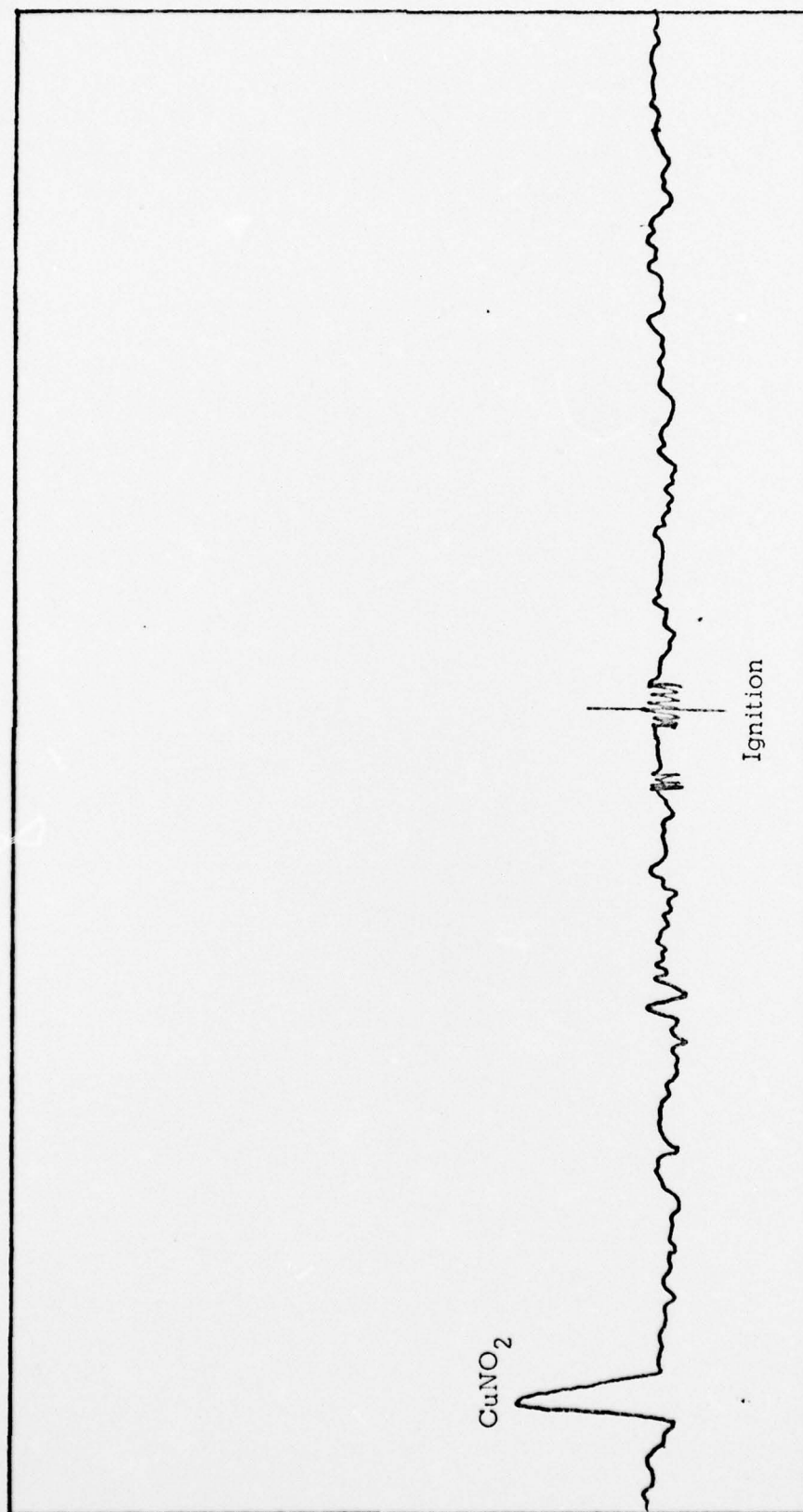Fig. 26. N-5 Propellant at Ignition

Fig. 27. HEX-12 Propellant at Ignition

Fig. 28. HEX-12 Propellant before and after Ignition

peaks are present in the amu range 70 to 110 until a strong peak at 110 corresponding to $CuNO_2$(g) is observed. No oxides or hydroxides are discernible above the noise level. Figure 29 shows the Pb and $PbNO_2$ peaks obtained from the HEX-12 propellant.

V.   SUMMARY

In assessing the experimental results obtained during the first three phases of the continuing studies on plateau burning propellant at this laboratory, several important facts may be briefly summarized.

1.   The study was made entirely of gas phase species. The reactions investigated included those on the burning surface, fizz zones, and the combustion area. These gas phase reactions and the chemistry involved allowed some conclusions to be made regarding the establishment of mechanisms for the plateau burning effect. Since the study was of gas phase species only, no attempt was made to establish the role played, if any, by the condensed phases for producing the plateau burning effect. However, the fact that the mass spectrometer studies of the decomposition of the lead organic salts established the formation of the metallic lead atom in both the gaseous and condensed phases does not conflict with the theory of Camp, et al,[11,12] that liquid metallic lead agglomerates form on the burning surface.

2.   The most significant result of this study is that the decomposition of the metallic additives results in the release of free gaseous metallic atoms which react with the nitrate esters to form $PbNO_2$ and $CuNO_2$. The formation of the gaseous metallic nitrite may be the chief criterion for the cause of the mesa effect.

3.   The $PbNO_2$ and $CuNO_2$ species, upon reaching the flame zone, react to form metallic oxides and hydroxides, as predicted by the thermodynamic equilibria, releasing an additional amount of energy.

4.   Although plateau burning propellants have previously been limited to employing metallic organic salts as additives, it is suggested that from the reactions taking place similar effects could be obtained by either a mixture of lead oxide and carbon black or the metallic element itself. The lead oxide and carbon black mixture would produce CO and Pb.
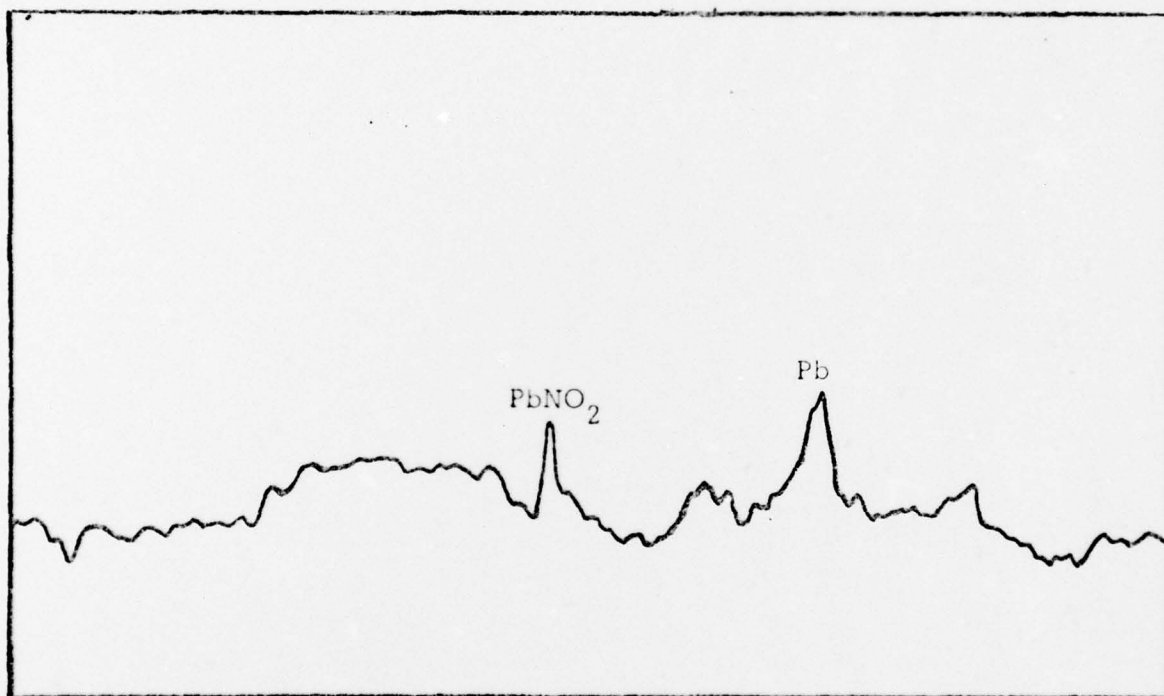
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Fig. 29. HEX-12 Propellant at Ignition

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Silver salicylate
Manganese salicylate
Mass spectroscopy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A mass spectrometer study has been conducted involving double base plateau burning propellants containing lead and copper organic salts. The pyrolysis and combustion of the metallic salts were also investigated. The results revealed that the metallic salts decompose to the gaseous and condensed phase metallic elements. The gaseous lead or copper atoms then react with the nitrate esters to form compounds such as $PbNO_2$ and $CuNO_2$, which are stable in the intermediate temperature zones. When the nitrites enter the combustion zone they react to produce the metallic hydroxides and oxides, as predicted by the thermodynamic equilibria.

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